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CAIO CÉSAR FERREIRA FLORINDO

MESOSCOPIC CONTINUUM THERMODYNAMICS FOR CHEMICAL SYSTEMS

TERMODINÂMICA MESOSCÓPICA DO CONTÍNUO PARA SISTEMAS QUÍMICOS

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Doctor´s dissertation presented to the Institute of Chemistry of the University of Campinas as part of the requirements to obtain the title of Doctor in Sciences.

Supervisor: Prof. Dr. Adalberto Bono Maurizio Sacchi Bassi

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Resumo

TERMODINÂMICA MESOSCÓPICA DO CONTÍNUO PARA SISTEMAS QUÍMICOS

Este trabalho utiliza a nova abordagem termodinâmica, chamada termodinâmica mesoscópica do contínuo, para descrever sistemas químicos onde as características microscópicas das partículas são levadas em conta. Explorando os conceitos da teoria constitutiva, um novo princípio de entropia é proposto para o espaço mesoscópico, o qual é semelhante àquele apresentado por Müller-Liu na termodinâmica dos meios contínuos macroscópica. Equações de balanço no espaço mesoscópico são obtidas para um ponto regular do sistema considerado. Tais equações diferem daquelas estabelecidas no espaço euclidiano tridimensional para o mesmo sistema, porque estas novas leis de balanço possuem termos adicionais advindos da diversidade topológica na qual a variável mesoscópica é definida. Em outras palavras, estas equações possuem termos que se originam das características microscópicas das partículas que compõem o sistema em estudo. Na modelagem constitutiva, foi empregado o método de multiplicadores de Lagrange proposto por Liu. O modelo constitutivo sugerido neste trabalho demonstrou ser fisicamente consistente e mais abrangente do que os modelos termodinâmicos usuais, visto que as expressões termodinâmicas por ele obtidas não se restringem nem a condições limites, nem ao equilíbrio. Portanto, a nova abordagem apresentada neste trabalho mostra-se muito promissora, uma vez que características microscópicas das partículas, descartadas na termodinâmica do contínuo tradicional, passam agora a desempenhar um papel importante no entendimento de sistemas químicos. Além disso, os resultados aqui apresentados podem ser estendidos para o estudo de materiais complexos, como por exemplo, ligas, cristais líquidos, fibras de carbonos, metamateriais, nano tubos e outros.

Palavras chaves: Teoria mesoscópica; Princípio de entropia; Multiplicadores de Lagrange; Termodinâmica dos meios contínuos.

Abstract

MESOSCOPIC CONTINUUM THERMODYNAMICS FOR CHEMICAL SYSTEMS

This work applies the new thermodynamic approach, called continuous mesoscopic thermodynamics, in order to describe chemical systems by taking into account the microscopic characteristics of the particles. Exploring the constitutive theory concepts, a new entropy principle for the mesoscopic space is proposed, which is similar to that presented by Müller-Liu in macroscopic continuum thermodynamics. Balance equations are obtained for a regular point of the system considered. Such equations are different from those established in three-dimensional Euclidean space for the same system, because they include additional terms arising from the topological manifold on which the mesoscopic variable is defined. In other words, these equations include terms arising from the microscopic features of the particles that compose the system under study. For constitutive modeling, the method of Lagrange multipliers proposed by Liu is employed. The constitutive model suggested here is physically consistent and covers a broader range of applications than usual thermodynamic models, since the thermodynamic expressions obtained are not restricted neither to limit conditions, nor to equilibrium. Therefore, this new approach is very promising, since microscopic features of the particles, discarded in traditional continuous thermodynamics, become now an important part in the understanding of chemical systems. In addition, the results presented here can be extended to the study of other complex materials such as alloys, liquid crystals, carbon fibers, meta-materials, nano-tubes etc.

keywords: Mesoscopic theory; Entropy principle; Lagrange multipliers; Continuum thermodynamics.

List of Figures

List of Symbols

$\boldsymbol{x}$	Material point
t	Time
N	N-*th* constituent of the mixture
$\mathfrak{B}$	Continuous body
$\mathcal{P}$	Part of the continuous body $\mathfrak{B}$
Δm	Mass of part $\mathcal{P}$
ΔV	Volume of part $\mathcal{P}$
$\rho_{average}$	Average density
ρ	Mass density
$s(\boldsymbol{x}, t)$	Macroscopic specific entropy
σ	Specific entropy production
η	Specific entropy supply
$\mathfrak{E}$	Entropy flux
$\mathfrak{B}_\alpha$	α-*th* constituent of the mixture
X_α	Particle or material point of $\mathfrak{B}_\alpha$
κ_α	Reference configuration of $\mathfrak{B}_\alpha$
G_α	Motion of each constituent α
$\mathcal{E}$	Euclidean space
$\boldsymbol{v}_\alpha$	Velocity of α
F_α	Deformation gradient of α
c_α	Mass concentration of α
$\boldsymbol{u}_\alpha$	Translational diffusion velocity of α
$\boldsymbol{s}_\alpha(\boldsymbol{x}, t)$	Macroscopic spin of α
$\boldsymbol{\omega}_\alpha(\boldsymbol{x}, t)$	Macroscopic local angular velocity of α
$\boldsymbol{I}_\alpha$	Inertia momentum tensor of α

Ψ	Arbitrary physical variable
$\mathfrak{B}_t$	Present configuration of continuum body $\mathfrak{B}$ at time t
$\mathfrak{B}_{ref}$	Reference configuration of continuum body $\mathfrak{B}$
$\mathcal{P}_t$	Part of $\mathfrak{B}_t$
$\partial\mathcal{P}_t$	Boundary of $\mathcal{P}_t$
$\mathscr{P}$	Production term
$\mathscr{S}$	Supply term
$\mathscr{F}$	Flux term
ϑ	Density of Ψ
$\psi(\boldsymbol{x}, t)$	Macroscopic field
$\psi(\cdot)$ or ψ	Mesoscopic field
$\mathbf{\Gamma}_\psi(\boldsymbol{x}, t)$	Non-convective flux of $\psi(\boldsymbol{x}, t)$ at a regular point
$\mathfrak{p}_\psi(\boldsymbol{x}, t)$	Macroscopic production term at a regular point
$\mathfrak{s}_\psi(\boldsymbol{x}, t)$	Macroscopic supply term at a regular point
$\mathfrak{p}_\psi(\cdot)$	Mesoscopic production term at a regular point
$\mathfrak{s}_\psi(\cdot)$	Mesoscopic supply term at a regular point
n	Outward unit normal vector
$\mathcal{A}$	Non-empty set
d	Metric of $\mathcal{A}$
x, y, z	Points of $\mathcal{A}$
$\mathbb{R}^n$	Euclidean n-space
ϵ	Radius of ball
$B_\epsilon(x)$	Open ball
$B_\epsilon[x]$	closed ball
$\mathbb{R}_+$	Positive real number
τ	Topology of $\mathcal{A}$
$\emptyset$	Empty set
A	Open subsets of $\mathcal{A}$
$\mathbb{Z}_+^*$	Set of non-zero and non-negative integers
φ	Homeomorphism
$\mathcal{A}_m$	Euclidean manifold
h	Injection function

$\mathbb{N}$	Natural numbers
$\boldsymbol{m}$	Set of mesoscopic variables
$\mathcal{D}^i$	Euclidean topological manifold with dimension i
$\mathcal{M}^n$	Mesoscopic space of dimension i
$\mathbb{R}^3$	Three-dimensional Euclidean space
$\mathbb{R}^1$	One-dimensional Euclidean space
$\mathfrak{X}$	Collection of open sets or basis
$f(\cdot)$	Mesoscopic distribution function (MDF)
$\mathfrak{S}^2$	Unit sphere manifold
$\boldsymbol{n}$	Microscopic director
$\mathfrak{R}_t$	Region in $\mathbb{R}^3 \times \mathfrak{S}^2$ at time t
$\Psi_{\mathfrak{R}_t}$	Physical variable in the mesoscopic space
$\Gamma^*_{\psi(\cdot)}$	Non-convective flux in $\mathfrak{S}^2$
$\boldsymbol{v}(\cdot)$	Mesoscopic material velocity
$\boldsymbol{w}(\cdot)$	Mesoscopic change velocity of $\boldsymbol{n}$
$\boldsymbol{j}_\alpha$	Diffusive flux of α
$\boldsymbol{h}_\alpha$	Rotational diffusive flux of α
$\boldsymbol{T}$	Cauchy stress tensor
$\boldsymbol{T}^*$	Cauchy stress tensor in $\mathfrak{S}^2$
$\boldsymbol{f}_\alpha$	Momentum supply density
$\boldsymbol{o}_\alpha$	Linear momentum production
$\boldsymbol{s}_\alpha$	Mesoscopic spin vector of α
$\boldsymbol{W}_\alpha$	Mesoscopic surface torque
$\boldsymbol{W}^*$	Mesoscopic surface torque in $\mathfrak{S}^2$
$\boldsymbol{g}_\alpha$	Angular momentum density
$\boldsymbol{i}_\alpha$	Production of spin
$\boldsymbol{t}_\alpha$	Dual vector
ε_α	Specific internal energy of α
$\boldsymbol{\phi}_\alpha$	Heat flux vector
$\boldsymbol{\phi}^*$	Heat flux vector in $\mathfrak{S}^2$
r_α	External radiation
$\mathfrak{e}_\alpha$	Internal energy production

$\mathfrak{G}_\alpha$	Micromorphic spin production of constituent α
$\mathfrak{E}^*$	Flux vector of entropy in $\mathfrak{S}^2$
χ_α	Production of mass
Λ^ρ	Lagrange multipliers of mass
Λ^{c_α}	Lagrange multipliers of concentration
$\Lambda^{\boldsymbol{v}}$	Lagrange multipliers of velocity
$\Lambda^{\boldsymbol{\omega}}$	Lagrange multipliers of angular velocity
Λ^ε	Lagrange multipliers of energy
p	Thermodynamic pressure
Θ	Absolute temperature
μ_α	Chemical potential of α
$\mathrm{grd}(\mu_\alpha)$	Reduced gradient of μ_α
$\mathfrak{F}_k$	Chemical affinity a reaction k
Ω_k	Rate of conversion of k
$\mathcal{Q}$	Helmholtz energy
ν	Specific volume
$\mathcal{G}$	Gibbs energy
C_p	Specific heat at constant pressure
C_ν	Specific heat at constant volume
λ	coefficient of thermal expansion
κ	Isothermal compressibility

Contents

Chapter 1

Introduction

1.1 Introduction

Continuum thermodynamics is a non-linear field theory of classical physics, which is concerned with deformations and motions of continuous material bodies[1] under the influence of mechanical, electromagnetic, thermal, and chemical sources [1]. Since mid-1960, the continuum approach for material bodies has been an important theoretical tool for engineers and applied mathematicians because it provides a very useful and reliable representation for macroscopic bodies whose characteristic dimensions are much bigger than the molecular ones. On the other hand, most of the chemists are still not aware of the methods of continuum thermodynamics as an alternative to traditional thermodynamic theories.

Continuum thermodynamics is built on two main grounds: (1) basic fields, which obey balance laws valid for all bodies regardless of their constitution and (2) specific equations for each body named constitutive laws [2]. Usually, in thermodynamics one considers only the basic fields mass, linear momentum, angular momentum, energy and entropy, but in special situations, for example, when microscopic characteristics of the system particles are taken into account, other basic fields need to be added. In this case, for materials with a more complicated internal structure than simple materials[2],

[1]The term material body will be employed whenever an abstract system is referred, which accepts the use of appropriate mathematical tools in an attempt to describe the observable real body. A material body is considered continuous if the volumetric density of mass may be spatially integrated. Note that, in this approach, the body constitution is characterized by an infinite number of points or particles, also known as primitive elements of that body. Thus, in continuum media, the particles are contained essentially within points on which a density may be defined.

[2]Materials consisting of spherical particles with interactions depending only on the inter-particle dis-

other variables need to be added for their unique description [3]. Some examples of such complex materials are steel, shape memory alloys, micro-cracks, liquid crystals, polymer melts, solutions and others [4].

In principle, there are two possibilities to include additional quantities into the continuum thermodynamics description: The first one is to introduce additional fields and their balance equations defined on space-time $(\boldsymbol{x}, t)$. This approach has a long history in continuum mechanics, starting with the Cosserat brothers [5, 6] in the early twentieth century and extending to current days [7, 8, 9, 10]. A second possibility is to introduce the concept of mesoscopic space [11], which historically stems from the theory of liquid crystals by taking into account the orientation distribution function of the molecules [12, 13, 14, 15, 16, 17]. In this approach, the additional quantities (also called mesoscopic variables) extend space-time to the so-called mesoscopic space. As a result, all other fields along with their respective balance equations are redefined in this new space. In spite of that, the balance equations can be easily written down on the mesoscopic space because only the number of dimensions change, in comparison with the usual balances on space-time $(\boldsymbol{x}, t)$.

A major advantage of the mesoscopic theory is to allow flexibility in defining the topological diversity, according to the internal structure (or internal degree of freedom) of the body of interest. Thus, if the internal structure is known, then the manifold nature becomes clear. The mesoscopic concept also introduces a statistical element, called mesoscopic distribution function (MDF), which is applied to the different values of mesoscopic variables into an infinitesimal volume. Although this concept inserts a distribution function, the theory itself is not microscopic in nature, because it is not assumed any kind of interaction between the particles, unlike what is done, for example, in the kinetic theory of gases. Commonly, the mesoscopic theory is allocated between the macroscopic and microscopic levels of description because it includes more information than a macroscopic theory, but less than a microscopic one on the molecular level. For this reason, this theory may be regarded as a bridge-theory that interconnects these two levels by investigating about how much the microscopic features of the particles affect the observed macroscopic data of the system, without detailing its molecular structure.

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tances.

The mesoscopic concept has been applied to a wide variety of materials hitherto, as for example, liquid crystals [11, 12, 13, 14, 15, 16, 17], micro-cracks [18, 19, 20], ferrofluids [21], granular materials [22], and to diffusion phenomena in mixtures [23]. However, there are no studies directly involving chemical systems yet. Even in macroscopic continuum thermodynamics there are very few works addressing this subject. Therefore, the aim of this work is to propose a general mesoscopic continuum model to describe complex chemical systems of N-constituents by using the mesoscopic concept. Although the proposed model focuses on a specific chemical system only, the results presented can be extended to study more complex ones, as polymer solutions, steels, crystal liquids, carbon fibers or nanotubes, etc.

1.2 Objectives

The purpose of this work is to develop a mesoscopic continuous model for describing complex chemical systems. One expects that the thermodynamic relations obtained in this work are natural consequences of the mesoscopic concept, and that they are valid for any thermodynamic state of the chemical system considered, either at equilibrium or not. Consequently, Lagrange multipliers are incorporated to the mesoscopic entropy balance equation, so that it must hold under no constraints for all admissible thermodynamic processes. In order to assess the implications of this model for chemical systems, some results are compared with those of classical thermostatics and with recent works in continuum thermodynamics.

1.3 Structure of Thesis

This thesis is divided into five chapters, including this introduction. Chapter 2 is devoted to the presentation of macroscopic continuum thermodynamics foundations. Particularly, attention is focused on the continuum concept, the different available continuum approaches, second law of thermodynamics, mixture theories, and the basic laws of physics in the context of macroscopic continuum thermodynamics. In Chapter 3, a topological mesoscopic theory is presented. The mesoscopic balances of mass, momentum, angular momentum, spin, total energy, internal energy and entropy are

written down and discussed. Moreover, a remark on how to recover the macroscopic balances from the mesoscopic balances is also presented. Chapter 4 is dedicated to the exploitation of thermodynamic restrictions on constitutive functions and their consequences for the chemical system proposed. Finally, in Chapter 5, some closing comments about the model are presented.

Chapter 2

Fundamentals of continuous thermodynamics

2.1 Continuum concept

The molecular nature of matter is a well established concept in science. However, various investigations of material behavior in areas such as, engineering, mechanics and the like, do not take into account the structure of the individual molecule. Indeed, such an approach is consistent and very useful, whenever the characteristic dimensions of the materials are extremely large compared to the distances between the molecules that compose it [24].

Usually, for material bodies the continuous concept is employed where the discrete nature of matter can be safely ignored. In this concept, one assumes that the substance of a body is distributed throughout, and completely fills the space it occupies. Although one may speak of a material body as "occupying" a region of physical space, it is evident that the body does not totally "fill" the space it occupies. However, acknowledging all due limitations on which the continuum approach remain valid, this concept provides a framework for studying the behavior of solids, liquids and gases. Suffice it to say that more than 200 years of experience have justified such an approach in a wide variety of situations [25].

Once the continuous approximation is considered, then one assumes that the matter is divided into smaller and smaller portions indefinitely, each of which retains all the physical properties of the original body. According to this, the physical field quantities

such as mass and energy volumetric densities, velocity, and others are assigned to every point of the region of space that the body occupies. Thus, the field quantities can be expressed as integrable functions of time and space.

It is worth emphasizing that in continuum thermodynamics, the punctual mass density field of a material body is a fundamental physical property assigned as a part of the specification of the continuous body [26]. In fact, the concept of punctual mass density is developed from mass-volume ratios in the neighborhood of a point $\boldsymbol{x}$ within a part $\mathcal{P}$ of the continuous body $\mathfrak{B}$, as can be seen in the figure below.

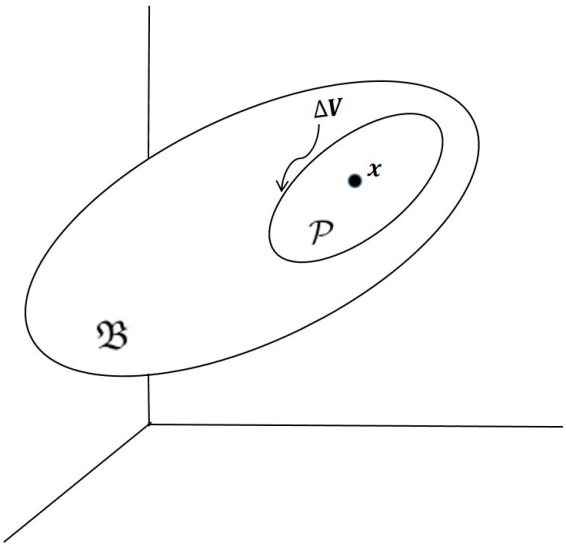

Figure 2.1: *Scheme showing how one defines the mass density ρ at any point $\boldsymbol{x}$ within a material body $\mathfrak{B}$.*

In figure above, the mass of part $\mathcal{P}$, denoted by Δm, occupies a volume ΔV, and thence, the average density of the material within ΔV can be defined by

$$\rho_{\text{average}} = \frac{\Delta m}{\Delta V}. \tag{2.1}$$

The density at some interior point $\boldsymbol{x}$ of the volume ΔV is given mathematically in accordance with the continuum concept by the limit,

$$\rho_{\text{point}} = \lim_{\Delta V \to 0} \frac{\Delta m}{\Delta V} = \frac{d\,m}{d\,V} > 0, \tag{2.2}$$

2.2 Development of Continuum Thermodynamics

Thermodynamics has in recent years experienced a fresh impetus mainly through several reorganizations of its basic postulates and applications in several areas. Extensions have not only been achieved on the level of irreversible thermodynamics, but also within the class of the so called rational thermodynamics (RT). In the following, some information about the different available continuum approaches is presented, starting from thermostatics and reaching RT, since the present theory combines ideas from some of these approaches.

Thermodynamics is an extension and outgrowth of 19th century thermostatics, or equilibrium thermodynamics. The latter is concerned with reversible processes, *i.e.* atemporal processes whose evolution can be reversed, and thereby, leading to another possible thermostatic process [27]. The first systematic theory dealing with irreversible processes was started in the year 1940 by C. Eckart who wrote two basic papers [28, 29]. In the following years the theory was completed by J. Meixner [30, 31], who studied the phenomenological coefficients in detail and equipped these with Onsager-Casimir reciprocal relations. Finally, in the 60s, S.R. de Groot and P. Mazur put together the previously proposed ideas in the fundamental monograph, *Non-equilibrium thermodynamics* [32]. The theory developed by these authors has been applied by many workers in the following decades and, it is still in broad use nowadays under the labeling thermodynamics of irreversible processes (TIP) [33].

The TIP cornerstone is the local equilibrium hypothesis. This hypothesis assume that the local and instantaneous relations among thermodynamic quantities in a system out of equilibrium are the same as if the system was in an equilibrium state. The TIP also considers that the system under study can be mentally split into a series of cells sufficiently large to allow them to be treated as macroscopic thermodynamic subsystems, but sufficiently small that equilibrium is very close to be realized in each cell [34]. Hence, variables such as temperature and entropy may be rigorously and unambiguously defined just as the cells were at equilibrium. While these two assumptions are well-motivated for small fluctuations of the local equilibrium state, they are not suitable for thermodynamic states far from the equilibrium [27, 35]. Indeed, statistical and kinetic analysis show that the local equilibrium hypothesis is consistent with instantaneous linear relations between fluxes and forces only.

In a wide variety of problems, the linearity assumption of the instantaneous constitutive relations is too stringent. This is particularly true in chemistry, rheology and other sciences. Another problem resides in phenomena involving short time and small space scales at which the velocity distribution of particles cannot be described by a Maxwell distribution function. In this case, the local-equilibrium hypothesis breakdown wholly. In addition, there are other TIP limitations that are not pointed out here [34]. Thus, in view of the theoretical and practical limitations of both equilibrium thermodynamics and TIP, efforts have been made to enlarge the range of application of non-equilibrium thermodynamics and, thereby, emerging a new theory, called rational thermodynamics (RT) by its authors.

The RT was mainly developed by Coleman, Noll and Truesdell, and it is currently known as continuum thermodynamics [36, 37, 38, 39, 40]. Such theory, shares some similar viewpoints with TIP. However, the RT follows a line of thought drastically different from TIP by taking into account new premises that are based on more general physical and mathematical principles valid for all types of bodies. In addition, in RT there is no assumption of equilibrium, neither for the whole system, nor for the point.

Basically, the RT purpose is to provide a method for deriving constitutive equations by following some basic assumptions:

- Absolute temperature and entropy are considered primitive concepts. They are introduced *a priori* and do not have a precise physical interpretation.

- The fundamental laws of physics, such as the balances of mass, linear momentum, energy and entropy must concern all bodies, independently of their particularities.

- The constitutive equations define the material behavior. Hence, one may conclude that an absolute material law can not be assigned to any material even though some aspects of its behavior with regard to driving processes can be described by equations of a certain form. This implies that, the selection of the constitutive independent variables is subordinated to the type of material one deals with.

- In order to ensure the constitutive model mathematical and physical coherence, material equations must obey some requirements of the constitutive theory, such

as material objectivity, material symmetry and the second law of thermodynamics. This requirements have been extensively discussed and detailed [1, 41], so that they will not be shown in this work.

- It is assumed that materials have a memory, i.e. the behavior of a system at a given instant of time is determined not only by the values of the parameters at present time, but also by their past history. Thus, the constitutive equations written in their general form involve functionals applied to the whole history of the variables. Such equations are not easily tractable and, generally they require the knowledge of too vast an amount of information. Consequently, the memory effect is not considered except in certain systems.

- The state of a material point may be influenced not only by processes arising at its immediate neighborhood, but by those occurring at all points of the body. This behavior accounts for non-local properties.

Even in RT, specially concerning its use in continuum mixtures, there are different formulations of the second law of thermodynamics and the source terms (also called supply terms) of the momentum and energy balance equations. So, it is worthwhile to address some comments about theses approaches. Within the formalism developed by Coleman and Noll in [36, 37, 38], unspecified source terms in the momentum and energy equations are required to guarantee that the state variables and their time derivatives can be varied independently, that is, their values can be arbitrarily varied without affecting the exploitation of the second law of thermodynamics. However, in normal circumstances, theses source terms are known from the start and they assume well-defined values. This limits seriously the domain of applicability of the RT developed by Coleman and Noll. Moreover, this approach has been shown to be inconsistent with some results of the gas kinetic theory and inappropriate to treat the diffusion theory of continuum mixtures, as demonstrated by Truesdell [39].

In view of the problems presented by the Coleman and Noll approach, Müller proposed a weaker formulation of the entropy principle [42, 43], which satisfies all necessary requirements of an irreversibility statement and reads as follows:

- In every material body there exists an additive quantity, the specific entropy $s(\boldsymbol{x}, t)$,

which obeys a balance equation for the mixture

$$\rho\sigma = \rho\frac{ds}{dt} + \operatorname{div}(\mathfrak{E}) - \rho\eta \geq 0, \tag{2.3}$$

in which $\mathfrak{E}$ is the entropy flux, η the specific entropy supply and σ the specific entropy production. Note that, for all thermodynamic processes, the specific entropy production for the mixture must be a non-negative quantity, $\sigma \geq 0$, but the entropy production for each constituent may take any value. The obtaining of (2.3) as well as the remaining balance equations will be presented in the next section.

- Entropy flux and supply are considered unspecified constitutive quantities.
- The nature of the restrictions imposed on the system behavior by the second law of thermodynamics is purely constitutive. Thus, by obtaining these restrictions the (external) supply terms that appear in all balance equations are omitted.
- There exists a special material singular surface between two continuous media, the so-called ideal wall, across which the (empirical) temperature and the tangential velocity are continuous.

The Müller approach was the first fundamental contribution to mixture theory. Later, the application of Lagrange multipliers for the exploitation of the entropy inequality was developed in Müller's research group by I-Shih Liu [44, 45]. Generally speaking, Liu's procedure involves the incorporation of Lagrange multipliers in the entropy inequality, so that it must hold under no constraints for all admissible thermodynamic processes. For a more detailed mathematical description of continuum thermodynamics with Lagrange multipliers, references [46] and [47] are suggested. An excellent overview has been provided by Bowen [48].

2.3 Mixture theory and Balance equations

The theories of mixtures in the framework of continuum thermodynamics were initiated in 1957 by a series of articles by Truesdell [39, 40, 49] and later, extended and corrected by Müller [42, 43, 44, 46, 50, 51, 52]. According to Truesdell's standpoint, a continuum mixture is formed by superposing constituents, such that each material point

is simultaneously occupied by particles of all constituents. Hence, each material point, which is assumed to be infinitesimal size, carries the local physical properties of the body under study. Note that the word "particles" in continuum theories do not represent atoms, molecules, or other classical particles, but mathematical points endowed with physical properties.

Truesdell also assumes that each constituent behaves as a single fluid and, by analogy, one may assign balance laws for the constituents as for single pure materials. It is taken for granted that the motion of a mixture is governed by the same equations as for a single body. Thus, the properties of constituents are considered as primitives quantities, and those of the mixture are formulated with basis in the characteristics of pure chemical substances.

2.3.1 Kinematics

Let $\mathfrak{B}$ be a mixture of N constituents $\mathfrak{B}_\alpha$, all of which are supposed to be able to occupy the same region of space simultaneously. A particle or material point of $\mathfrak{B}_\alpha$ is represented by X_α, so that $\alpha = 1, ..., N$, being the index N reserved for the solvent. Thus, if one assume κ_α as a reference configuration of $\mathfrak{B}_\alpha$ and denote $B_\alpha = \kappa_\alpha(\mathfrak{B}_\alpha)$, then the motion of $\mathfrak{B}_\alpha$ is a smooth mapping in form

$$G_\alpha : B_\alpha \times \mathbb{R} \to \mathcal{E}, \quad \boldsymbol{x} = G_\alpha(\boldsymbol{X}_\alpha, t), \quad \boldsymbol{X}_\alpha \in B_\alpha, \tag{2.4}$$

which states that for different motion G_α of each constituent, at the same instant t, there is a material point $X_\alpha \in \mathfrak{B}_\alpha$ represented in the reference configuration by $\boldsymbol{X}_\alpha = \kappa_\alpha(X_\alpha)$, that occupies the same spatial position $\boldsymbol{x}$ in the Euclidean space $\mathcal{E}$ [53].

Each constituent has its own kinematics. So, thereby, the velocity and deformation gradient of each constituent α can be defined, respectively, as

$$\boldsymbol{v}_\alpha = \frac{\partial}{\partial t} G_\alpha(\boldsymbol{X}_\alpha, t), \quad F_\alpha = \frac{\partial}{\partial \boldsymbol{X}_\alpha} G_\alpha(\boldsymbol{X}_\alpha, t). \tag{2.5}$$

$\mathfrak{B}_\alpha$ has its own mass and, hence, a positive mass density $\rho_\alpha(\boldsymbol{x}, t)$ at each point $\boldsymbol{x}$ and time t. Thus, one may related the mass density of the whole mixture $\rho(\boldsymbol{x}, t)$ with

$\rho_\alpha(\boldsymbol{x}, t)$,

$$\rho(\boldsymbol{x}, t) = \sum_\alpha \rho_\alpha(\boldsymbol{x}, t). \tag{2.6}$$

Likewise, one also defines the mass concentration of $\mathfrak{B}_\alpha$,

$$c_\alpha = \frac{\rho_\alpha}{\rho}, \tag{2.7}$$

that implies $\sum_\alpha c_\alpha = 1$. The mean velocity of body $\mathfrak{B}$ is defined by

$$\rho \boldsymbol{v} = \sum_\alpha \rho_\alpha \boldsymbol{v}_\alpha, \tag{2.8}$$

and the translational diffusion velocity of $\mathfrak{B}_\alpha$,

$$\boldsymbol{u}_\alpha = \boldsymbol{v}_\alpha - \boldsymbol{v}, \tag{2.9}$$

where $\sum_\alpha \rho_\alpha \boldsymbol{u}_\alpha = 0$.

In order to consider the microscopic structure of mixtures into the continuum model, it is necessary to include new kinematic variables associated to each point $(\boldsymbol{x}, t)$ of the mixture. Thus, if the mechanics of rigid bodies is assumed, each constituent particle possesses a spin field $\boldsymbol{s}(\boldsymbol{x}, t)$ and a local angular velocity $\boldsymbol{\omega}_\alpha(\boldsymbol{x}, t)$. These two field quantities are interrelated by

$$\boldsymbol{s}_\alpha = \boldsymbol{I}_\alpha \boldsymbol{\omega}_\alpha, \tag{2.10}$$

in which $\boldsymbol{I}_\alpha$ represents the inertia momentum tensor. All these quantities can be also extended to the mixture particle, such that one has

$$\rho \boldsymbol{s} = \sum_\alpha \rho_\alpha \boldsymbol{s}_\alpha, \quad \rho \boldsymbol{I} \boldsymbol{\omega} = \sum_\alpha \rho_\alpha \boldsymbol{I}_\alpha \boldsymbol{\omega}_\alpha, \quad \rho \boldsymbol{I} = \sum_\alpha \rho_\alpha \boldsymbol{I}_\alpha. \tag{2.11}$$

2.3.2 Forms of the Balance equations

One of the main objectives of continuum thermodynamics is to calculate the motions of the particles forming the continuum bodies, and the evolution of field quantities as density, temperature, energy, etc. Generally, this can be done by means of functional differential equations together with appropriate initial and boundary conditions.

These equations covers two sets of statements, the so-called balance equations and the constitutive relations. The present section is devoted to the presentation and description of balance equations only. For a detailed mathematical derivation of theses equations, references [1, 54] are suggested.

Let Ψ be a physical variable which characterizes a partial aspect of the state of the continuum body $\mathfrak{B}_t$ at time t. According to the continuum hypothesis, the variable Ψ is defined by some equation analogous to (2.2), *i.e.*, as a density per unit volume or area at every regular point $\boldsymbol{x}$ within ΔV (see figure 2.1). Besides, the variable Ψ in $\mathfrak{B}$ may change in time according to three possible different effects:

1. Production $\mathscr{P}$ - This quantity is produced inside the body itself, for example, production of heat in a body due to radioactive decay. Another interesting example is chemical reactions in a solution.

2. Supply $\mathscr{S}$- The supply or source density is exclusively caused by action from outside the body, at a distance from it, so that the whole volume of $\mathfrak{B}$ is directly affects. Example: gravitation affects the momentum of a body.

3. Flux $\mathscr{F}$- The fluxes, also called surface densities, are actions transmitted from the outside into the body through its surface. Examples: stress on the surface of a body and heat flux through a surface.

Thus, the time rate of change of the variable Ψ of the body $\mathfrak{B}$ per unit time may be written as

$$\frac{d\Psi}{dt} = \mathscr{P}_\psi + \mathscr{S}_\psi + \mathscr{F}_\psi. \tag{2.12}$$

By using the transport theorem [47], one can write the above equation as

$$\frac{\partial \psi}{\partial t} + \operatorname{div}\left(\psi \otimes \boldsymbol{v} + \boldsymbol{\Gamma}_\psi\right) = \mathfrak{s}_\psi + \mathfrak{p}_\psi, \tag{2.13}$$

where,

$$\Psi = \int_{\mathcal{P}_t} \psi(\boldsymbol{x}, t) dV, \quad \mathscr{P}_\psi = \int_{\mathcal{P}_t} \mathfrak{p}_\psi(\boldsymbol{x}, t) dV, \mathscr{S}_\psi = \int_{\mathcal{P}_t} \mathfrak{s}_\psi(\boldsymbol{x}, t) dV, \quad \mathscr{F}_\psi = \int_{\partial\mathcal{P}_t} \boldsymbol{\Gamma}_\psi(\boldsymbol{x}, t) \mathbf{n} dA,$$

are equivalent to a sum of individual contributions for all particles contained in a part $\mathcal{P}_t$ of $\mathfrak{B}_t$. Here, dV and dA are the volume and area differentials, respectively, and **n** is the

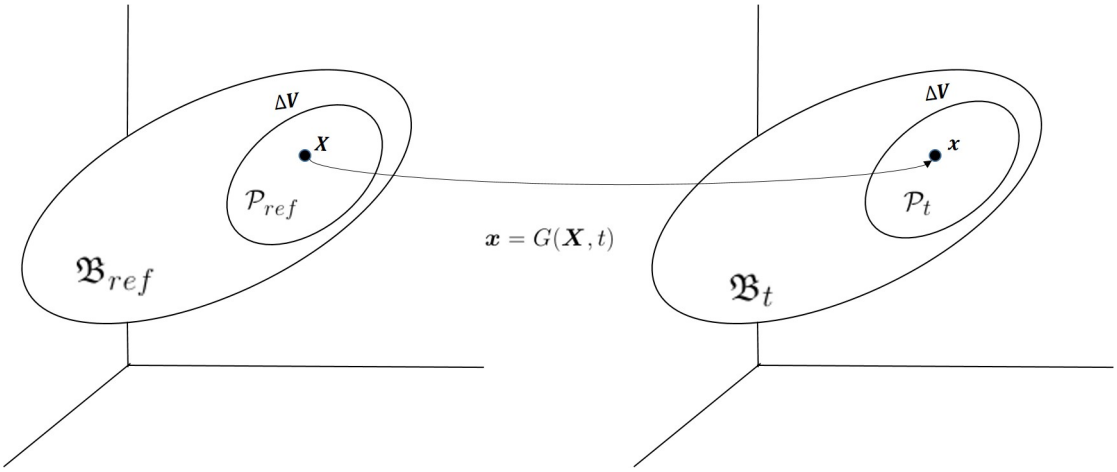

Figure 2.2: *Material domains in the reference and present configurations.* $\mathfrak{B}_{ref}$ *and* $\mathfrak{B}_t$ *are material bodies in the reference and present configurations, respectively.* $\boldsymbol{x} = G(\boldsymbol{X}, t)$ *is the motion of the body.*

outward unit normal vector to the boundary $\partial\mathcal{P}_t$ of the region $\mathcal{P}_t$, at the same boundary point $\boldsymbol{x}$ referred by $\boldsymbol{\Gamma}_\psi(\boldsymbol{x}, t)$.

The statement (2.12) is the global balance form for a physical variable in the Euler representation (present configuration, see fig.2.2)[1] incorporating the additivity principle for an arbitrary material part $\mathcal{P}_t$ of $\mathfrak{B}_t$. While (2.13) is the local balance equation in the Euler representation valid at a regular point $\boldsymbol{x} \in \mathcal{P}_t \subseteq \mathfrak{B}_t$. Note that, if the body is isolated, $\mathscr{S} = 0$ and $\mathscr{F} = 0$. Then, $\mathscr{P} = 0$, Ψ is constant in time and, thereby, Ψ is said to be a conserved quantity.

2.3.3 Special balance equations

As already mentioned, a thermodynamic system is characterized by the specification of mass, momentum, angular momentum, energy and entropy, therefore balance laws

[1] In fluid mechanics there are two different mathematical representations of fluid flow: Lagrangian representation in which one follows all fluid particles and describes the variations around each fluid particle along its trajectory. The other is Eulerian, where the variations are described at all fixed coordinates as a function of time. For example: Let ϑ be the density of Ψ assigned to every material point in the reference configuration and let ψ denote the corresponding density in the present configuration. Further, we choose an open set $\mathcal{P}_{ref}$ of a body $\mathfrak{B}_{ref}$ with its bounding surface $\partial\mathcal{P}_{ref}$ in the reference configuration (see fig.2.2).

In present configuration, the part of $\mathfrak{B}_t$ and the boundary surface are $\mathcal{P}(t)$ and $\partial\mathcal{P}(t)$, respectively, which are explicitly dependent on time. Thus, the value of the physical variable Ψ at time t is obtained by the additivity principle, i.e., by volume integration of ϑ and ψ.

$$\Psi = \int_{\mathcal{P}_t} \psi(\boldsymbol{x}, t) dV, \qquad \Psi = \int_{\mathcal{P}_{ref}} \vartheta(\boldsymbol{X}, t) dV.$$

must be stated for these five quantities. These equations can be easily derived from (2.13) and already has been discussed by many authors, however, for the sake of convenience, they are outlined below. It is noteworthy that the equations will be defined in form of material derivative $d^\alpha\psi_\alpha/dt = \partial\psi_\alpha/\partial t + \boldsymbol{v}_\alpha \cdot \mathrm{grad}(\psi_\alpha)$ following the motion of the constituent α.

First, we shall write down the balance laws for each constituent α of a reacting mixture and then, for the whole mixture. So, one has

Mass Balance:

The balance equation for mass can be obtained with substitutions

$$\psi = \rho_\alpha(\boldsymbol{x}, t), \quad \boldsymbol{\Gamma}_{(\rho)} = 0, \quad \mathfrak{s}_{(\rho)} = 0, \quad \mathfrak{p}_{(\rho)} = \chi_\alpha(\boldsymbol{x}, t)$$

in (2.13) yielding the final forms of the local mass balance for constituent α

$$\frac{d^\alpha\rho_\alpha}{dt} + \rho_\alpha \,\mathrm{div}(\boldsymbol{v}_\alpha) - \chi_\alpha = 0. \tag{2.14}$$

For the whole solution one has

$$\frac{d\rho}{dt} + \rho \,\mathrm{div}(\boldsymbol{v}) = 0. \tag{2.15}$$

where $\chi = \sum_\alpha \chi_\alpha = 0$, $\rho = \sum_\alpha \rho_\alpha$, $\rho\boldsymbol{v} = \sum_\alpha \rho_\alpha \boldsymbol{v}_\alpha$.

Linear Momentum:

Replacing

$$\psi = \rho_\alpha \boldsymbol{v}_\alpha, \quad \boldsymbol{\Gamma} = -\boldsymbol{T}_\alpha, \quad \mathfrak{s} = \rho_\alpha \boldsymbol{f}_\alpha, \quad \mathfrak{p} = \boldsymbol{o}_\alpha$$

in (2.13) yields

$$\rho_\alpha \frac{d^\alpha \boldsymbol{v}_\alpha}{dt} - \mathrm{div}\,(\boldsymbol{T}_\alpha) = \rho_\alpha \boldsymbol{f}_\alpha + (\boldsymbol{o}_\alpha - \boldsymbol{v}_\alpha \chi_\alpha), \tag{2.16}$$

where $\boldsymbol{T}_\alpha$ is the Cauchy stress tensor, $\rho_\alpha \boldsymbol{f}_\alpha$ is the momentum supply density exercised by external forces into the system and $\boldsymbol{o}_\alpha$ the linear momentum production of the other constituents of the solution for the constituent α. It follows for the solution that

$$\rho\frac{d\boldsymbol{v}}{dt} - \operatorname{div}(\boldsymbol{T}) = \rho\boldsymbol{f}, \tag{2.17}$$

where,

$$\sum_{\alpha}(\boldsymbol{o}_\alpha - \boldsymbol{v}_\alpha\chi_\alpha) = 0, \quad \rho\boldsymbol{f} = \sum_{\alpha}\rho_\alpha\boldsymbol{f}_\alpha,$$
$$\boldsymbol{T} = \sum_{\alpha}\boldsymbol{T}_\alpha - \sum_{\alpha}\rho_\alpha\boldsymbol{u}_\alpha\otimes\boldsymbol{u}_\alpha.$$

Spin and angular velocity:

Let

$$\psi = \rho_\alpha\boldsymbol{s}_\alpha + \boldsymbol{x}\times\rho_\alpha\boldsymbol{v}_\alpha, \quad \boldsymbol{\Gamma} = -\boldsymbol{x}\times\boldsymbol{T}_\alpha - \boldsymbol{W}_\alpha, \quad \mathfrak{s} = \boldsymbol{x}\times\rho_\alpha\boldsymbol{f}_\alpha + \rho\boldsymbol{g}_\alpha, \quad \mathfrak{p} = \boldsymbol{x}\times\boldsymbol{o}_\alpha + \boldsymbol{i}_\alpha.$$

Then, starting from the balances of linear and total angular momentum, and mass, the spin balance can be deduced. For constituent α, the spin balance equation is given by

$$\rho_\alpha\frac{d^\alpha\boldsymbol{s}_\alpha}{dt} - \operatorname{div}(\boldsymbol{W}_\alpha) - \boldsymbol{t}_\alpha = \rho_\alpha\boldsymbol{g}_\alpha + \boldsymbol{i}_\alpha - \boldsymbol{s}_\alpha\chi_\alpha. \tag{2.18}$$

Here, $\boldsymbol{s}_\alpha$ is the spin vector, $\boldsymbol{W}_\alpha$ the couple stress , $\rho_\alpha\boldsymbol{g}_\alpha$ is the angular momentum density exerted by external forces on the spin $\boldsymbol{s}_\alpha$, and $\boldsymbol{i}_\alpha$ the production of spin. The dual vector $\boldsymbol{t}_\alpha$ corresponds to the antisymmetric part of the stress tensor $\boldsymbol{T}$, which is closely related to the microscopic structure of the mixture. In fact, if microscopic structure effects on the macroscopic motion in the Euclidean space are not considered, $\boldsymbol{T}$ is symmetric.

Considering the definition of spin $\boldsymbol{s}_\alpha = \boldsymbol{I}_\alpha\boldsymbol{\omega}_\alpha$ and the mixture as a micro-polar medium, then $d^\alpha\boldsymbol{I}_\alpha/dt = 0$. Hence, one obtains the balance of angular velocity of the constituent α,

$$\rho_\alpha\boldsymbol{I}_\alpha\frac{d^\alpha\boldsymbol{\omega}_\alpha}{dt} - \operatorname{div}(\boldsymbol{W}_\alpha) - \boldsymbol{t}_\alpha = \rho_\alpha\boldsymbol{g}_\alpha + \boldsymbol{i}_\alpha - \boldsymbol{I}_\alpha\boldsymbol{\omega}_\alpha\chi_\alpha. \tag{2.19}$$

Thus, for the solution one has

$$\rho \boldsymbol{I} \frac{d\boldsymbol{\omega}}{dt} - \operatorname{div}(\boldsymbol{W}) - \boldsymbol{t} = \rho \boldsymbol{g}, \tag{2.20}$$

where,

$$\rho \boldsymbol{I} = \sum_{\alpha} \rho_{\alpha} \boldsymbol{I}_{\alpha}, \quad \boldsymbol{I}\boldsymbol{\omega} = \sum_{\alpha} \boldsymbol{I}_{\alpha}\boldsymbol{\omega}_{\alpha}, \quad \sum_{\alpha} (\boldsymbol{i}_{\alpha} - \boldsymbol{I}_{\alpha}\boldsymbol{\omega}_{\alpha}\chi_{\alpha}) = 0$$
$$\rho \boldsymbol{g} = \sum_{\alpha} \rho_{\alpha} \boldsymbol{g}_{\alpha}, \quad \boldsymbol{t} = \sum_{\alpha} \boldsymbol{t}_{\alpha}, \quad \boldsymbol{W} = \sum_{\alpha} \boldsymbol{W}_{\alpha} - \sum_{\alpha} \rho_{\alpha} \boldsymbol{s}_{\alpha} \otimes \boldsymbol{u}_{\alpha}.$$

Internal energy

From

$$\psi = \rho_{\alpha}\varepsilon_{\alpha} + \frac{1}{2}\rho_{\alpha}\boldsymbol{v}_{\alpha}\cdot\boldsymbol{v}_{\alpha} + \frac{1}{2}\rho_{\alpha}\boldsymbol{s}_{\alpha}\cdot\boldsymbol{\omega}_{\alpha}, \qquad \boldsymbol{\Gamma} = -\boldsymbol{v}_{\alpha}\boldsymbol{T}_{\alpha}^{T} - \boldsymbol{\omega}_{\alpha}\boldsymbol{W}_{\alpha}^{T} + \boldsymbol{\phi}_{\alpha}$$
$$\mathfrak{s} = \boldsymbol{v}_{\alpha}\cdot\rho_{\alpha}\boldsymbol{f}_{\alpha} + \boldsymbol{w}_{\alpha}\cdot\rho\boldsymbol{g}_{\alpha} + \rho\, r_{\alpha}, \qquad \mathfrak{p} = \mathfrak{e}_{\alpha},$$

one has for the constituent α

$$\rho_{\alpha}\frac{d^{\alpha}\varepsilon_{\alpha}}{dt} + \operatorname{div}(\boldsymbol{\phi}_{\alpha}) - \boldsymbol{T}_{\alpha}^{T} : \operatorname{grad}(\boldsymbol{v}_{\alpha}) - \boldsymbol{W}_{\alpha}^{T} : \operatorname{grad}(\boldsymbol{\omega}_{\alpha})$$
$$+\boldsymbol{\omega}_{\alpha}\cdot[(\boldsymbol{i}_{\alpha} - \chi_{\alpha}\boldsymbol{s}_{\alpha}) - \boldsymbol{t}_{\alpha}] + \boldsymbol{v}_{\alpha}\cdot(\boldsymbol{o}_{\alpha} - \boldsymbol{v}_{\alpha}\chi_{\alpha})$$
$$+\chi_{\alpha}\left(\varepsilon_{\alpha} + \frac{1}{2}\boldsymbol{v}_{\alpha}\cdot\boldsymbol{v}_{\alpha} + \frac{1}{2}\boldsymbol{s}_{\alpha}\cdot\boldsymbol{\omega}_{\alpha}\right) + \frac{1}{2}\rho_{\alpha}\left(\boldsymbol{\omega}_{\alpha}\cdot\frac{d^{\alpha}\boldsymbol{s}_{\alpha}}{dt} - \boldsymbol{s}_{\alpha}\cdot\frac{d^{\alpha}\boldsymbol{\omega}_{\alpha}}{dt}\right) = \rho_{\alpha}r_{\alpha} + \mathfrak{e}_{\alpha}. \tag{2.21}$$

In this equation, ε_{α} is the specific internal energy and $\boldsymbol{\phi}_{\alpha}$ is heat flux vector. The scalar r_{α} is the supply related to external radiation and $\mathfrak{e}_{\alpha}$ the internal energy production. The others supplies do not appear because they are included in some terms of the above equation, as will be shown in appendix B. One has

$$\rho\frac{d\varepsilon}{dt} + \operatorname{div}(\boldsymbol{\phi}) - \boldsymbol{T}^{T} : \operatorname{grad}(\boldsymbol{v}) - \boldsymbol{W}^{T} : \operatorname{grad}(\boldsymbol{\omega}) - \boldsymbol{\omega}\cdot\boldsymbol{t} = \rho r, \tag{2.22}$$

for the solution, where

$$\sum_\alpha \mathfrak{e}_\alpha = 0, \quad \mathfrak{G}_\alpha = \frac{1}{2}\rho_\alpha \left(\boldsymbol{\omega}_\alpha \cdot \frac{d^\alpha \boldsymbol{s}_\alpha}{dt} - \boldsymbol{s}_\alpha \cdot \frac{d^\alpha \boldsymbol{\omega}_\alpha}{dt} \right) = 0, \quad \boldsymbol{z}_\alpha = \boldsymbol{\omega}_\alpha - \boldsymbol{\omega}$$

$$\rho\, r = \sum_\alpha \left(\rho_\alpha r_\alpha + \boldsymbol{u}_\alpha \cdot \rho_\alpha \boldsymbol{f}_\alpha + \boldsymbol{z}_\alpha \cdot \rho_\alpha \boldsymbol{g}_\alpha \right), \quad \rho\varepsilon = \sum_\alpha \left(\rho_\alpha \varepsilon_\alpha + \frac{1}{2}\rho_\alpha \boldsymbol{u}_\alpha \cdot \boldsymbol{u}_\alpha + \frac{1}{2}\rho_\alpha \boldsymbol{s}_\alpha \cdot \boldsymbol{z}_\alpha \right),$$

$$\boldsymbol{\phi} = \sum_\alpha \left[\boldsymbol{\phi}_\alpha - \boldsymbol{u}_\alpha \boldsymbol{T}_\alpha^T - \boldsymbol{z}_\alpha \boldsymbol{W}_\alpha^T + \left(\rho_\alpha \varepsilon_\alpha + \frac{1}{2}\rho_\alpha \boldsymbol{u}_\alpha \cdot \boldsymbol{u}_\alpha + \frac{1}{2}\rho_\alpha \boldsymbol{s}_\alpha \cdot (\boldsymbol{z}_\alpha - \boldsymbol{\omega}) \right) \boldsymbol{u}_\alpha \right].$$

Entropy principle

By following Müller's propositions, the entropy balance for constituent α can be formulated as

$$\rho_\alpha \frac{d^\alpha s_\alpha}{dt} = -\mathrm{div}\left(\mathfrak{E}_\alpha \right) + \rho_\alpha \eta_\alpha + \rho_\alpha \sigma_\alpha, \tag{2.23}$$

where s_α is the specific entropy, η_α is the entropy supply, σ_α the entropy production, and $\mathfrak{E}$ the flux vector of entropy. The entropy production for a single constituent is not definite. Thus, dissipation inequalities do not exist for single constituents, thereby the dissipation inequality for the solution of all constituents can be formulated only, namely

$$\rho\sigma = \rho \frac{ds}{dt} + \mathrm{div}\left(\mathfrak{E} \right) - \rho\eta \geq 0. \tag{2.24}$$

Here,

$$\rho\, s = \sum_\alpha \rho_\alpha\, s_\alpha, \quad \rho\eta = \sum_\alpha \rho_\alpha \eta_\alpha, \quad \rho\sigma = \sum_\alpha \rho_\alpha \sigma_\alpha.$$

All these balance equations previously shown are fundamental physical laws that are valid for all bodies irrespective of their constitution and unalterable within the domain of classical mechanics.

Chapter 3

Mesoscopic space

In order to define the mesoscopic space, it is necessary first to introduce some basic concepts about topological spaces. In this section, only some fundamental concepts on this subject are presented, while other basic definitions are placed in appendix A. However, if the reader is interested in a more detailed mathematical description about topological spaces, references [55, 56] are suggested.

3.1 Topological fundamentals

This section begins with a short text on the metric space[1]. It is important to discuss this space beforehand, because topological objects as open and closed sets may be defined, by induction, from the metric space concept. Such sets are fundamental objects for studying more abstract topological spaces, as will be demonstrated in the following sections.

3.1.1 Metric space

The metric space is a set where some distance function between all its members is defined. The specific distance function is called a metric on the set. Normally, one describes the metric space like the ordered pair ($\mathcal{A}$, d), where $\mathcal{A}$ is a non-empty set and d is its metric. This metric must satisfy the following conditions: $\forall x, y, z \in \mathcal{A}$, so one has,

[1] Every metric space is a topological space, and therefore all definitions and theorems about general topological spaces also apply to all metric spaces.

- $d(x, y) = 0 \Leftrightarrow x = y$, identity of a indiscernible;
- $d(x, y) \geq 0$, non-negativity;
- $d(x, y) = d(y, x)$, symmetry;
- $d(x, y) \leq d(x, z) + d(z, y)$, triangle inequality;

In order to better understand such conditions, the following examples may be helpful:

1. Discrete metric:

$$d(x, y) = \begin{cases} 1 & \text{if } x \neq y, \\ 0 & \text{if } x = y \end{cases}$$

2. Euclidean n-space, $\mathbb{R}^n$:

$$d(x, y) = \sqrt{(x_1 - y_1)^2 + ... + (x_n - y_n)^2} = \left[\sum_{i=1}^{n} (x_i - y_i)^2\right]^{1/2}. \qquad (3.1)$$

In general, a metric $d(x, y)$ may induce topological properties in the subsets of $\mathcal{A}$. Hence, if one wishes to impose certain characteristics on the subsets of $\mathcal{A}$, then it is necessary to establish *a priori* some metric within $\mathcal{A}$. For example, to define subsets of $\mathcal{A}$ as open or closed balls, initially a metric relative to the radius ϵ of the balls must be considered, as follows.

Definition 3.1 *Let ($\mathcal{A}$, d) be a metric space. So, the open and closed (metric) balls of radius $\epsilon > 0$ centered at a point x_0 in $\mathcal{A}$, denoted by $B_\epsilon(x)$ and $B_\epsilon[x]$, respectively, are defined by*

$$B_\epsilon(x) = \{x \in \mathcal{A} : d(x, x_0) < \epsilon\} \quad \textit{and} \quad B_\epsilon[x] = \{x \in \mathcal{A} : d(x, x_0) \leq \epsilon\}, \qquad (3.2)$$

where the point $x_0 \in \mathcal{A}$ and ϵ is a positive real number $\epsilon \in \mathbb{R}_+$. The open ball $B_\epsilon(x)$ is an open set (for the definitions of open and closed sets see Appendix A-1).

3.1.2 Topological space

The most popular way to define a topological space is in terms of open sets. Indeed, the fundamental structure of a topological space is not a distance function, but a collections of open sets[2].

Let $\mathcal{A}$ and τ be a nonempty set and its topology, respectively. Hence, τ is a family (collection) of open subsets of $\mathcal{A}$ that satisfies the following properties:

- $\emptyset$, $\mathcal{A} \in \tau$.
- If A_1, $A_2 \in \tau$, so $A_1 \cup A_2 \in \tau$, where A_1 and A_2 are any arbitrary collections.
- Given a finite arbitrary family $(A_i)_{i \in \mathbb{Z}_+^*}$, $\forall i \in \mathbb{Z}_+^*$ with $A_i \in \tau$ one has $(\cap A_i) \in \tau$, where $\mathbb{Z}_+^*$ is the set of positive integers.

Thus, a topological space ($\mathcal{A}$, τ) consists of two objects: a non-empty arbitrary set $\mathcal{A}$ and a topology τ at $\mathcal{A}$. Typically, one denotes a topological space ($\mathcal{A}$, τ) just like $\mathcal{A}$, since its topology is known, while the elements of $\mathcal{A}$ are called points. If the open sets are open balls or unions of them, then the topology τ at $\mathcal{A}$ is induced by a metric, and the space is said to be metrizable.

In the study of unfamiliar topological spaces, usually different types of isomorphism between these spaces and a known topological space are employed, so that the properties of the new spaces can be studied. In this section, a special type of isomorphism is highlighted, namely, the homeomorphism. Briefly, homeomorphism[3] is a continuous function between two topological spaces, which also has a continuous inverse function. Hence, a function $\varphi : \mathcal{A} \to \mathcal{B}$ between two topological spaces $(\mathcal{A}, \tau_{\mathcal{A}})$ and $(\mathcal{B}, \tau_{\mathcal{B}})$ is called a homeomorphism if it has the following properties:

- φ is a bijection function
- φ is continuous function with the inverse function φ^{-1} also continuous, so that φ is an open map[4].

[2]There are other ways to define a topological space (for example, using closed sets), but by means of the open sets, it is easier and more intuitive to understand.

[3]A classic example in topology suggests that a doughnut and coffee cup are indistinguishable from the topological point of view. This happens, because one of the geometric objects can be stretched and bent continuously from the other.

[4]An open map is a function between two topological spaces which maps open sets to open sets.

Thus, homeomorphisms are functions that preserve all the topological properties of a given space to another, such that, if a topological space $\mathcal{A}$ is homeomorphic to a space $\mathcal{B}$, then they are equal topologically.

Euclidean topological manifold

The presented definition of topological space $\mathcal{A}$ is a very general one that encompasses an important class of abstract objects commonly studied, the so-called Euclidean topological manifolds. A Euclidean manifold $\mathcal{A}_m$ is also a topological space, although, it has some additional specifications:

- $\mathcal{A}_m$ is a Hausdorff space, that is, $\mathcal{A}_m$ is a topological space where distinct points have disjoint neighborhoods[5]. Thus, $\forall x, y \in \mathcal{A}_m, x \neq y : \exists U, V \in \tau : x \in U, y \in V : U \cap V = \emptyset$.

- $\mathcal{A}_m$ is second-countable space, that is, the topology $\tau \in \mathcal{A}_m$ is finite or countably infinite[6].

- $\mathcal{A}_m$ is locally Euclidean of dimension n, that is, the neighborhood of every point in $\mathcal{A}_m$ is homeomorphic to an open subset of $\mathbb{R}^n$.

It is worthwhile mentioning that there are other kinds of manifolds, such as the soft, Riemannian, Finslerian and others. However, in this work, we will use only the Euclidean topological manifold to define the mesoscopic space.

[5]For any two distinct elements $x, y \in \mathcal{A}_m$ there exist disjoint open sets $U, V \in \tau_{\mathcal{A}}$ containing x and y respectively, *i.e*, U and V have no elements in common.

[6]A space is said to be second-countable if its topology has a countable base. More explicitly, this means that $\mathcal{A}$ is countable if and only if there exists an injection, $h : \mathcal{A} \to \mathbb{N}$, where $\mathbb{N}$ is the set of all natural numbers.

3.2 Mesoscopic concept

There are four patterns to build a topological space: subspaces, product spaces, disjoint union and quotient spaces. In this work, the concept of product spaces[7] is adopted to define the mesoscopic space. The concept presented here is quite general and it attempts to encompass those used in references [12, 15, 16, 22, 23, 57, 58, 59, 60, 61, 62].

Definition 3.2 *Let $\boldsymbol{m} \in \mathcal{D}^i$ be a set of additional variables in an Euclidean topological manifold $\mathcal{D}^i$ with dimension i, on which an integration can be defined. So, one defines the mesoscopic space $\mathcal{M}$ of dimension $n = i + 4$ by*

$$\mathcal{M}^n = \mathcal{D}^i \times \mathbb{R}^3 \times \mathbb{R}^1, \quad \textit{where} \quad (\boldsymbol{m}, \boldsymbol{x}, t) \in \mathcal{M}^n. \tag{3.3}$$

Here, the manifold $\mathcal{D}$ is given by the set $\boldsymbol{m}$, which represents the values of the internal degrees of freedom of the system. Hence, the choice of $\mathcal{D}$ depends of the complex system under consideration, but if the internal structure is known, then the nature of $\mathcal{D}$ is clear.

Note that $\mathcal{D}^i \subset \mathcal{E}$ is a subset of the Euclidean space similar to $\mathbb{R}^3$ and $\mathbb{R}^1$, thereby, it is reasonable to consider that the topology τ generated in the mesoscopic space $\mathcal{M}^n$ is Euclidean. At first sight, this conclusion seems to be trivial, because the mesoscopic space $\mathcal{M}^n$ itself is a subset of the Euclidean space. However, the proof of this statement is not so obvious. In fact, its demonstration requires the concept of product topology generated by a basis of open sets (see Appendix A-2).

Let $(\mathcal{M}, \tau_{\mathcal{M}})$ be a topological mesoscopic space. A collection $\mathfrak{X}$ of open sets is called a base (or basis) for the topology $\tau_{\mathcal{M}}$ if every open set $A \subseteq \mathcal{M}$ included in the topology $\tau_{\mathcal{M}}$ is the union of sets in $\mathfrak{X}$. Obviously, $\tau_{\mathcal{M}}$ is a base for itself. Thus, one assumes a special base $\mathfrak{X}$ that satisfies the following two properties:

- The base elements cover $\mathcal{M}$ *i.e,* $\mathcal{M} = \bigcup_{A \in \mathfrak{X}} A$. Note that this condition is equivalent to the statement that the union of all sets in $\mathfrak{X}$ is $\mathcal{M}$.

- If $A_1, A_2 \in \mathfrak{X}$ and $x \in A_1 \cap A_2$, then there is an $A \in \mathfrak{X}$ such that $x \in A \subseteq A_1 \cap A_2$.

[7] A product space is the Cartesian product of topological manifolds equipped with a standard topology. See the following text for the concept of standard topology and Appendix A-2 for a short justification about this concept.

If $\mathfrak{X}$ satisfies both of the two conditions, then there is a standard topology $\tau_{\mathcal{M}}$ on $\mathcal{M}$ for which $\mathfrak{X}$ is a base. For example, the collection of all open intervals in the real line forms a base for a standard topology on the real line because the intersection of any two open intervals is itself an open interval or empty. The same argument is also valid for the mesoscopic space, where the collection of all open subsets in $\mathcal{M} = \mathcal{D}^i \times \mathbb{R}^3 \times \mathbb{R}^1$ forms a base $\mathfrak{X}$ for a standard topology $\tau_{\mathcal{M}}$ of $\mathcal{M}$. Hence, as all the manifolds $\mathcal{D}^i$, $\mathbb{R}^3$ and $\mathbb{R}^1$ are Euclidean, then a standard topology $\tau_{\mathcal{M}}$ in $\mathcal{M}$, generated by $\mathfrak{X}$, is Euclidean as well.

3.2.1 Mesoscopic distribution function

The mesoscopic concept also introduces a mesoscopic distribution function (MDF)

$$f(\boldsymbol{m}, \boldsymbol{x}, t) \equiv f(\cdot), \qquad (\cdot) \equiv (\boldsymbol{m}, \boldsymbol{x}, t) \in \mathcal{M}^n. \tag{3.4}$$

This function describes the distribution of $\boldsymbol{m}$ on $\boldsymbol{x}$ at time t, and thereby, it is always normalized

$$\int f(\boldsymbol{m}, \boldsymbol{x}, t)\, d\mathcal{D} = 1. \tag{3.5}$$

In particular, the mesoscopic mass density $\rho(\cdot)$ is defined by using the MDF and macroscopic mass density $\rho(\boldsymbol{x}, t)$,

$$\rho(\cdot) := \rho(\boldsymbol{x}, t) f(\boldsymbol{m}, \boldsymbol{x}, t), \quad \text{where} \quad \rho(\boldsymbol{x}, t) = \int \rho(\cdot)\, d\mathcal{D}. \tag{3.6}$$

This equation shows that the system can be formally treated as a mixture by regarding all particles presenting the same mesoscopic variables as one component of the system having the partial mass density $\rho(\cdot)$ into an infinitesimal volume around $\boldsymbol{x}$ at time t. It is also worthwhile noting that the relation (3.6) is analogous to the well-known formula of mixture theory

$$\rho = \sum_{\alpha} \rho_{\alpha}, \tag{3.7}$$

which states that the mass density of a mixture is the sum of the mass densities of its constituents at a regular[8] point of the system, at any time. In this sense, one may

[8] At a regular point all considered fields are derivable and their derivatives are continuous.

consider mesoscopic theory as a mixture theory, where the "component index" $\boldsymbol{m}$ is continuously describing the various species. Other mesoscopic fields can be also obtained in addition to the mass density, as for example, mesoscopic material velocity $\boldsymbol{v}(\cdot)$, mesoscopic spin $\boldsymbol{s}(\cdot)$, energy $\varepsilon(\cdot)$ etc. All theses mesoscopic fields obey mesoscopic balance equations that will be formulated later.

The MDF allows the calculation of macroscopic order parameters that represent additional fields to those introduced in the conventional theory. Moreover, it also can be used as an approximation method to obtain some experimental properties of liquid crystals [63].

3.3 General constitutive assumptions

Once the concept of mesoscopic space is presented, then one can define the characteristics that the system under study assumes in this space.

In this work, the system is regarded as a material solution formed by N constituents. The constituents are considered rigid, and they possess a planar shape, or they are needle-shaped. To justify this physical imposition, the unit sphere manifold $\mathfrak{S}^2 \subseteq \mathcal{D}$ is assumed. This manifold represents the space in which both the shape and orientation of the particles are defined. The orientation of particles is determined by the microscopic director $\boldsymbol{n} \in \mathfrak{S}^2$, which is defined as a unit vector pointing in the temporary direction of a planar or needle-shaped rigid particle. This director is defined on a molecular level and, consequently represents a mesoscopic variable, which spans the 2-dimensional unit sphere $\mathfrak{S}^2$. Thus, for this reason, the mesoscopic space used in this work is the product space $\mathcal{M}^6 = \mathfrak{S}^2 \times \mathbb{R}^3 \times \mathbb{R}^1$, wherein the homeomorphism $\varphi : \mathfrak{S}^2 \longrightarrow \mathbb{R}^2$ allows treatment of $\mathfrak{S}^2$ as $\mathbb{R}^2$ (see Appendix A-3).

In the present investigation, the solution obeys the postulates of the classical theory of mixtures[9] proposed by Truesdell, Müller and Liu, and all fields are given in the Eulerian description. Specifically, the solution is treated as an aqueous diluted mixture

[9] It seems plausible to assume that an observer, who looks at the body as a whole and is not aware that it is composed of a number of constituents, will recognize this body as a one-component material and impose the postulates of a one-component continuum. This suggest that the balance laws for the solution as a whole must be conservation laws [1]. In order to realize this principle, it is necessary that the variables for the solution as a whole are related to the variables of the constituents by summing over all N constituents.

constituted by different chemical species, so that the main fluid (solvent) is much more dominant than all other constituents. A non-specified constituent is denoted by an index α, which assumes values $\alpha = 1, ..., N$, being N reserved for the solvent. Note that, in opposition to usual models, this one does not rule out chemical reactions.

3.4 Mesoscopic balance equations

Let $\mathfrak{R}_t$ denote a region in $\mathbb{R}^3 \times \mathfrak{S}^2$ at time t, and let a mesoscopic field $\psi(\cdot)$ symbolize the density of a quantity $\Psi_{\mathfrak{R}_t} = \int_{\mathfrak{R}_t} \psi(\cdot) dV\, d\mathfrak{S}^2$ to be balanced in $\mathfrak{R}_t$, where $(\cdot) \equiv (\boldsymbol{n}, \boldsymbol{x}, t) \in \mathcal{M}^6$. Then, by using the same argument made in the macroscopic space (see chapter 2), one can state that $\Psi_{\mathfrak{R}_t}$ changes due to a flux over the boundary $\partial\mathfrak{R}_t$ of $\mathfrak{R}_t$, which is composed by the fluxes $\Gamma_{\psi(\cdot)}$ and $\Gamma^*_{\psi(\cdot)}$ in $\mathbb{R}^3$ and $\mathfrak{S}^2$ respectively, a supply $\mathfrak{s}_{\psi(\cdot)}$ and a production $\mathfrak{p}_{\psi(\cdot)}$ within $\mathfrak{R}_t$, according to

$$\frac{d}{d\,t}\int_{\mathfrak{R}_t} \psi(\cdot) dV\, d\mathfrak{S}^2 = \int_{\partial\mathfrak{R}_t} \left[\Gamma_{\psi(\cdot)} + \Gamma^*_{\psi(\cdot)}\right] \mathbf{n} dA + \int_{\mathfrak{R}_t} \mathfrak{p}_{\psi(\cdot)} dV\, d\mathfrak{S}^2 + \int_{\mathfrak{R}_t} \mathfrak{s}_{\psi(\cdot)} dV\, d\mathfrak{S}^2, \quad (3.8)$$

where integrations expand over the mesoscopic space. By using a generalized Reynolds transport theorem [62], one can obtain the general balance expression for a regular point within mesoscopic space $\mathcal{M}^6$

$$\frac{\partial}{\partial t}\psi(\cdot) + \mathrm{div}[\psi(\cdot)\boldsymbol{v}(\cdot) + \Gamma_{\psi(\cdot)}] + \nabla_{\boldsymbol{n}} \cdot [\psi(\cdot)\boldsymbol{w}(\cdot) + \Gamma^*_{\psi(\cdot)}] = \mathfrak{s}_{\psi(\cdot)} + \mathfrak{p}_{\psi(\cdot)}. \quad (3.9)$$

Here, $\boldsymbol{v}(\cdot)$ is the mesoscopic material velocity in $\mathbb{R}^3$, and $\boldsymbol{w}(\cdot)$ is the mesoscopic change velocity of the microscopic director $\boldsymbol{n}$ in $\mathfrak{S}^2$.

The homeomorphism $\varphi : \mathfrak{S}^2 \longrightarrow \mathbb{R}^2$ allows treatment of $\mathfrak{S}^2$ as $\mathbb{R}^2$, thence, the properties of the divergence, gradient and other operators, well defined in the two-dimensional Euclidean space $\mathbb{R}^2$, can also be employed in the unit sphere manifold $\mathfrak{S}^2$. The symbol (div) is used when the divergence operator is applied on three-dimensional Euclidean space $\mathbb{R}^3$, but $(\nabla_{\boldsymbol{n}}\cdot)$ refer to the divergence operator on unit sphere manifold $\mathfrak{S}^2$. For the gradient operator, (grad) is used in $\mathbb{R}^3$ and (∇) in $\mathfrak{S}^2$.

The physical identification of the field $\psi(\cdot)$ depends on the balance considered. If $\psi(\cdot)$ is a scalar field, as for example the mass density one, $\Gamma_{\psi(\cdot)}$ and $\Gamma^*_{\psi(\cdot)}$ are vectors.

But if $\psi(\cdot)$ is a vector field, as for example the linear momentum density one, $\Gamma_{\psi(\cdot)}$ and $\Gamma^{*}_{\psi(\cdot)}$ are second order tensors and $\psi(\cdot)\boldsymbol{v}(\cdot)$ is the tensor product of the vectors $\psi(\cdot)$ and $\boldsymbol{v}(\cdot)$, usually written as $\psi(\cdot) \otimes \boldsymbol{v}(\cdot)$, and likewise $\psi(\cdot)\boldsymbol{w}(\cdot)$ as $\psi(\cdot) \otimes \boldsymbol{w}(\cdot)$. Note that the vector field $\rho\boldsymbol{x} \times \boldsymbol{v}$ is the angular momentum density at point $\boldsymbol{x}$ due to the movement of the fluid, while the spin density $\rho\boldsymbol{s}$ at the same point is a macroscopic effect caused by the internal structure of the system.

It is worthwhile highlighting that the mesoscopic mass density, as well as all other fields, are distinctive for different chemical constituents. If chemical reaction occurs, the total mass of the solution is a conservative quantity, while the mass of each constituent, in particular, is not. Analogously for the balances of linear and total angular momenta, and energy. Therefore, production terms related to the creation and annihilation emerge in these balance equations for constituents, but such terms are not present in the corresponding balance equations for the whole solution.

The balance equations obtained in this study are similar to those of references [12, 15, 16, 22, 23, 57, 58, 59, 60, 61, 62], except the mesoscopic concentration balance, which was not taken into account in the references aforementioned. However, in this work the balance equations are presented in a different way. Indeed, the concept of material derivative $d^{\alpha}Y_{\alpha}(\cdot)/dt$, where $Y_{\alpha}(\cdot)$ is the density of some system property for constituent α, is used (for example, $d^{\alpha}\rho_{\alpha}(\cdot)/dt = \partial\rho_{\alpha}(\cdot)/\partial t + \boldsymbol{v}_{\alpha}(\cdot) \cdot \mathrm{grad}[\rho_{\alpha}(\cdot)] + \boldsymbol{w}_{\alpha}(\cdot) \cdot \nabla[\rho_{\alpha}(\cdot)]$). The mathematical deductions of these balances are presented in Appendix B-2. For simplicity, in the balance equations the symbol $(\cdot)$ will be omitted. Thus, the balances for the constituents and the solution (mixture) follow.

Mass

For the constituent α

$$\frac{d^{\alpha}\rho_{\alpha}}{dt} + \rho_{\alpha}\,\mathrm{div}(\boldsymbol{v}_{\alpha}) + \rho_{\alpha}\,\nabla_{\boldsymbol{n}} \cdot (\boldsymbol{w}_{\alpha}) - \chi_{\alpha} = 0, \tag{3.10}$$

in which χ_{α} refers to the mass production of constituent α. For the whole solution one has

$$\frac{d\rho}{dt} + \rho\,\mathrm{div}(\boldsymbol{v}) + \rho\,\nabla_{\boldsymbol{n}} \cdot (\boldsymbol{w}) = 0, \tag{3.11}$$

where $\sum_{\alpha}\chi_{\alpha} = 0$, $\rho = \sum_{\alpha}\rho_{\alpha}$, $\rho\boldsymbol{v} = \sum_{\alpha}\rho_{\alpha}\boldsymbol{v}_{\alpha}$ and $\rho\boldsymbol{w} = \sum_{\alpha}\rho_{\alpha}\boldsymbol{w}_{\alpha}$.

Concentration

For constituent α

$$\rho\frac{dc_\alpha}{dt} + \operatorname{div}(\boldsymbol{j}_\alpha) + \nabla_{\boldsymbol{n}} \cdot (\boldsymbol{h}_\alpha) - \chi_\alpha = 0, \tag{3.12}$$

where $c_\alpha = \rho_\alpha/\rho$ is the mass concentration of constituent α, $\boldsymbol{j}_\alpha = \rho_\alpha \boldsymbol{u}_\alpha$ (for $\boldsymbol{u}_\alpha = \boldsymbol{v}_\alpha - \boldsymbol{v}$) is the diffusive flux of this constituent on $\mathbb{R}^3$ and $\boldsymbol{h}_\alpha = \rho_\alpha \boldsymbol{\varpi}_\alpha$ (for $\boldsymbol{\varpi}_\alpha = \boldsymbol{w}_\alpha - \boldsymbol{w}$) is the rotational diffusive flux on $\mathfrak{S}^2$. For the solution one has

$$\sum_{\alpha=1}^{N-1}\left[\rho\frac{dc_\alpha}{dt} + \operatorname{div}(\boldsymbol{j}_\alpha) + \nabla_{\boldsymbol{n}} \cdot (\boldsymbol{h}_\alpha) - \chi_\alpha\right] = 0. \tag{3.13}$$

Linear momentum

For the constituent α

$$\rho_\alpha\frac{d^\alpha \boldsymbol{v}_\alpha}{dt} - \operatorname{div}(\boldsymbol{T}_\alpha) - \nabla_{\boldsymbol{n}} \cdot (\boldsymbol{T}^*_\alpha) = \rho_\alpha \boldsymbol{f}_\alpha + (\boldsymbol{o}_\alpha - \boldsymbol{v}_\alpha \chi_\alpha), \tag{3.14}$$

where $\boldsymbol{T}_\alpha$ is the Cauchy stress tensor, $\boldsymbol{T}^*_\alpha$ its analogue defined in $\mathfrak{S}^2$, $\rho_\alpha \boldsymbol{f}_\alpha$ is the momentum supply density exercised by external force into the system and $\boldsymbol{o}_\alpha$ the linear momentum production of the other constituents of the solution for the constituent α. It follows for the solution that

$$\rho\frac{d\boldsymbol{v}}{dt} - \operatorname{div}(\boldsymbol{T}) - \nabla_{\boldsymbol{n}} \cdot (\boldsymbol{T}^*) = \rho \boldsymbol{f}, \tag{3.15}$$

where,

$$\sum_{\alpha=1}^{N}(\boldsymbol{o}_\alpha - \boldsymbol{v}_\alpha \chi_\alpha) = 0, \quad \rho\boldsymbol{f} = \sum_{\alpha=1}^{N}\rho_\alpha \boldsymbol{f}_\alpha,$$

$$\boldsymbol{T} = \sum_{\alpha=1}^{N}\boldsymbol{T}_\alpha - \sum_{\alpha=1}^{N}\rho_\alpha \boldsymbol{u}_\alpha \otimes \boldsymbol{u}_\alpha, \qquad \boldsymbol{T}^* = \sum_{\alpha=1}^{N}\boldsymbol{T}^*_\alpha - \sum_{\alpha=1}^{N}\rho_\alpha \boldsymbol{\varpi}_\alpha \otimes \boldsymbol{\varpi}_\alpha.$$

Angular velocity

Starting from the balances of linear and total angular momentum, and mass, the spin balance can be deduced. However, another balance equation can also be deduced from these, namely, the angular velocity balance. For constituent α, the spin balance equation is given by

$$\rho_\alpha \frac{d^\alpha \boldsymbol{s}_\alpha}{dt} - \operatorname{div}(\boldsymbol{W}_\alpha) - \nabla_{\boldsymbol{n}} \cdot (\boldsymbol{W}^*_\alpha) - \boldsymbol{t}_\alpha = \rho_\alpha \boldsymbol{g}_\alpha + \boldsymbol{i}_\alpha - \boldsymbol{s}_\alpha \chi_\alpha. \tag{3.16}$$

Here, $\boldsymbol{s}_\alpha$ is the spin vector, $\boldsymbol{W}_\alpha$ the mesoscopic surface torque or coupled stress on $\mathbb{R}^3$ and $\boldsymbol{W}^*$ its analogous on $\mathfrak{S}^2$, $\rho_\alpha \boldsymbol{g}_\alpha$ is the angular momentum density exerted by external forces on the mesoscopic spin $\boldsymbol{s}_\alpha$, and $\boldsymbol{i}_\alpha$ the production of spin. The dual vector $\boldsymbol{t}_\alpha$ is defined in $\mathbb{R}^3$. This vector corresponds to the antisymmetric part of the stress tensor $\boldsymbol{T}$. The existence of an antisymmetric part of the stress tensor has been closely related to the microscopic structure of the solution.

Considering the definition of spin $\boldsymbol{s}_\alpha = \boldsymbol{I}_\alpha \boldsymbol{\omega}_\alpha$ (do not confuse the spin angular velocity $\boldsymbol{\omega}$ defined in $\mathbb{R}^3$ with the change velocity $\boldsymbol{w}$ of the microscopic director $\boldsymbol{n} \in \mathfrak{S}^2$) and the mixture as a micro-polar medium[10], then $d^\alpha \boldsymbol{I}_\alpha / dt = 0$. Hence, one obtains the angular velocity balance of constituent α,

$$\rho_\alpha \boldsymbol{I}_\alpha \frac{d^\alpha \boldsymbol{\omega}_\alpha}{dt} - \operatorname{div}(\boldsymbol{W}_\alpha) - \nabla_{\boldsymbol{n}} \cdot (\boldsymbol{W}^*_\alpha) - \boldsymbol{t}_\alpha = \rho_\alpha \boldsymbol{g}_\alpha + \boldsymbol{i}_\alpha - \boldsymbol{I}_\alpha \boldsymbol{\omega}_\alpha \chi_\alpha. \tag{3.17}$$

Thus, for the solution one has

$$\rho \boldsymbol{I} \frac{d\boldsymbol{\omega}}{dt} - \operatorname{div}(\boldsymbol{W}) - \nabla_{\boldsymbol{n}} \cdot (\boldsymbol{W}^*) - \boldsymbol{t} = \rho \boldsymbol{g}, \tag{3.18}$$

[10] A constituent α is called micro-polar if its specific tensor of inertia is materially constant.

where,

$$\rho\boldsymbol{I} = \sum_{\alpha=1}^{N} \rho_\alpha \boldsymbol{I}_\alpha, \quad \rho\boldsymbol{I}\omega = \sum_{\alpha=1}^{N} \rho_\alpha \boldsymbol{I}_\alpha \boldsymbol{\omega}_\alpha, \quad \sum_{\alpha=1}^{N} (\boldsymbol{i}_\alpha - \boldsymbol{I}_\alpha \boldsymbol{\omega}_\alpha \chi_\alpha) = 0$$

$$\rho\boldsymbol{g} = \sum_{\alpha=1}^{N} \rho_\alpha \boldsymbol{g}_\alpha, \quad \boldsymbol{t} = \sum_{\alpha=1}^{N} \boldsymbol{t}_\alpha$$

$$\boldsymbol{W} = \sum_{\alpha=1}^{N} \boldsymbol{W}_\alpha - \sum_{\alpha=1}^{N} \rho_\alpha \boldsymbol{s}_\alpha \otimes \boldsymbol{u}_\alpha, \quad \boldsymbol{W}^* = \sum_{\alpha=1}^{N} \boldsymbol{W}_\alpha^* - \sum_{\alpha=1}^{N} \rho_\alpha \boldsymbol{s}_\alpha \otimes \boldsymbol{\varpi}_\alpha.$$

Internal energy

For constituent α one has

$$\rho_\alpha \frac{d^\alpha \varepsilon_\alpha}{dt} + \operatorname{div}(\boldsymbol{\phi}_\alpha) + \nabla_{\boldsymbol{n}} \cdot (\boldsymbol{\phi}_\alpha^*) - \boldsymbol{T}_\alpha^T : \operatorname{grad}(\boldsymbol{v}_\alpha) - \boldsymbol{W}_\alpha^T : \operatorname{grad}(\boldsymbol{\omega}_\alpha) - (\boldsymbol{T}_\alpha^*)^T : \nabla(\boldsymbol{v}_\alpha)$$
$$- (\boldsymbol{W}_\alpha^*)^T : \nabla(\boldsymbol{\omega}_\alpha) + \omega_\alpha \cdot [(\boldsymbol{i}_\alpha - \chi_\alpha \boldsymbol{s}_\alpha) - \boldsymbol{t}_\alpha] + \boldsymbol{v}_\alpha \cdot (\boldsymbol{o}_\alpha - \boldsymbol{v}_\alpha \chi_\alpha)$$
$$+\chi_\alpha \left(\varepsilon_\alpha + \frac{1}{2}\boldsymbol{v}_\alpha \cdot \boldsymbol{v}_\alpha + \frac{1}{2}\boldsymbol{s}_\alpha \cdot \boldsymbol{\omega}_\alpha \right) + \frac{1}{2}\rho_\alpha \left(\boldsymbol{\omega}_\alpha \cdot \frac{d^\alpha \boldsymbol{s}_\alpha}{dt} - \boldsymbol{s}_\alpha \cdot \frac{d^\alpha \boldsymbol{\omega}_\alpha}{dt} \right) = \rho_\alpha r_\alpha + \mathfrak{e}_\alpha. \quad (3.19)$$

In this equation ε_α is the specific internal energy, $\boldsymbol{\phi}_\alpha$ and $\boldsymbol{\phi}_\alpha^*$ are heat flux vectors defined in $\mathbb{R}^3$ and $\mathfrak{S}^2$, respectively. The scalar r_α is the supply related to external radiation and $\mathfrak{e}_\alpha$ the internal energy production. It is worth mentioning that $\mathfrak{G}_\alpha = \frac{1}{2}\rho_\alpha \left(\boldsymbol{\omega}_\alpha \cdot \frac{d^\alpha \boldsymbol{s}_\alpha}{dt} - \boldsymbol{s}_\alpha \cdot \frac{d^\alpha \boldsymbol{\omega}_\alpha}{dt} \right)$ is the micromorphic spin production of constituent α, but for a micro-polar continuum it vanishes. Thus, $\mathfrak{G}_\alpha$ will be null in the above equation. Considering such omission, one has

$$\rho \frac{d\varepsilon}{dt} + \operatorname{div}(\boldsymbol{\phi}) + \nabla_{\boldsymbol{n}} \cdot (\boldsymbol{\phi}^*) - \boldsymbol{T}^T : \operatorname{grad}(\boldsymbol{v}) - \boldsymbol{W}^T : \operatorname{grad}(\boldsymbol{\omega}) - (\boldsymbol{T}^*)^T : \nabla(\boldsymbol{v})$$
$$- (\boldsymbol{W}^*)^T : \nabla(\boldsymbol{\omega}) - \boldsymbol{\omega} \cdot \boldsymbol{t} = \rho r, \quad (3.20)$$

for the solution, where

$$\sum_{\alpha=1}^{N} \mathfrak{e}_\alpha = 0, \quad \mathfrak{G}_\alpha = \frac{1}{2}\rho_\alpha \left(\boldsymbol{\omega}_\alpha \cdot \frac{d^\alpha \boldsymbol{s}_\alpha}{dt} - \boldsymbol{s}_\alpha \cdot \frac{d^\alpha \boldsymbol{\omega}_\alpha}{dt} \right) = 0$$

$$\rho r = \sum_{\alpha=1}^{N} \left(\rho_\alpha r_\alpha + \boldsymbol{u}_\alpha \cdot \rho_\alpha \boldsymbol{f}_\alpha + \boldsymbol{z}_\alpha \cdot \rho_\alpha \boldsymbol{g}_\alpha \right), \quad \rho\varepsilon = \sum_{\alpha=1}^{N} \left(\rho_\alpha \varepsilon_\alpha + \frac{1}{2}\rho_\alpha \boldsymbol{u}_\alpha \cdot \boldsymbol{u}_\alpha + \frac{1}{2}\rho_\alpha \boldsymbol{s}_\alpha \cdot \boldsymbol{z}_\alpha \right),$$

$$\boldsymbol{\phi} = \sum_{\alpha=1}^{N} \left[\boldsymbol{\phi}_\alpha - \boldsymbol{u}_\alpha \boldsymbol{T}_\alpha^T - \boldsymbol{z}_\alpha \boldsymbol{W}_\alpha^T + \left(\rho_\alpha \varepsilon_\alpha + \frac{1}{2}\rho_\alpha \boldsymbol{u}_\alpha \cdot \boldsymbol{u}_\alpha + \frac{1}{2}\rho_\alpha \boldsymbol{s}_\alpha \cdot (\boldsymbol{z}_\alpha - \boldsymbol{\omega}) \right) \boldsymbol{u}_\alpha \right],$$

$$\boldsymbol{\phi}^* = \sum_{\alpha=1}^{N} \left[\boldsymbol{\phi}_\alpha^* - \boldsymbol{u}_\alpha \boldsymbol{T}_\alpha^T - \boldsymbol{z}_\alpha \boldsymbol{W}_\alpha^T + \left(\rho_\alpha \varepsilon_\alpha + \frac{1}{2}\rho_\alpha \boldsymbol{u}_\alpha \cdot \boldsymbol{u}_\alpha + \frac{1}{2}\rho_\alpha \boldsymbol{s}_\alpha \cdot (\boldsymbol{z}_\alpha - \boldsymbol{\omega}) \right) \boldsymbol{w}_\alpha \right].$$

Here, $\boldsymbol{z}_\alpha = \boldsymbol{\omega}_\alpha - \boldsymbol{\omega}$ was used to obtain the above relations (See Appendix B-2).

Entropy

In this work, a mesoscopic entropy balance slightly different than the macroscopic one is proposed to deduce the second law restrictions on the system behavior. However, we will assume beforehand some of the propositions used by Müller in the macroscopic entropy balance, such as:

- The entropy production for each constituent may take any value, whereas the entropy production of the whole mixture is a non-negative quantity.
- Entropy flux and supply are considered unspecified constitutive quantities.
- The nature of the restrictions imposed on the system behavior by the second law of thermodynamics is purely constitutive. Thus, by obtaining these restrictions the (external) supply terms that appear in all balance equations are omitted.

Hence, the mesoscopic entropy balance for constituent α is formulated as

$$\rho_\alpha \frac{d^\alpha s_\alpha}{dt} = -\mathrm{div}\left(\mathfrak{E}_\alpha\right) - \nabla_{\boldsymbol{n}} \cdot \left(\mathfrak{E}_\alpha^*\right) + \rho_\alpha \eta_\alpha + \rho_\alpha \sigma_\alpha, \tag{3.21}$$

where η_α is the entropy supply, σ_α the entropy production, and $\mathfrak{E}$ and $\mathfrak{E}^*$ are the flux vectors of entropy in $\mathbb{R}^3$ and $\mathfrak{S}^2$, respectively. By following the first proposition, dis-

sipation inequalities do not exist for single constituents and, thereby, the dissipation inequality for the solution of all constituents can be formulated only, namely

$$\rho\sigma = \rho\frac{ds}{dt} + \operatorname{div}(\mathfrak{E}) + \nabla_{\boldsymbol{n}} \cdot (\mathfrak{E}^*) - \rho\eta \geq 0. \tag{3.22}$$

Here,

$$\rho\, s = \sum_{\alpha=1}^{N} \rho_\alpha\, s_\alpha, \quad \rho\eta = \sum_{\alpha=1}^{N} \rho_\alpha \eta_\alpha, \quad \rho\sigma = \sum_{\alpha=1}^{N} \rho_\alpha \sigma_\alpha$$
$$\mathfrak{E} = \sum_{\alpha=1}^{N} \left(\mathfrak{E}_\alpha + s_\alpha \boldsymbol{u}_\alpha\right), \quad \mathfrak{E}^* = \sum_{\alpha=1}^{N} \left(\mathfrak{E}^*_\alpha + s_\alpha \boldsymbol{\varpi}_\alpha\right).$$

Note that all these balance equations are more complex than the macroscopic balances presented in Chapter 2. Nevertheless, they carry much more information about the microscopic characteristics of the particles than any macroscopic balance equation. Moreover, such mesoscopic equations directly reflect the influence of the shape and orientation of the particles in the solution under study.

3.5 Mesoscopic to macroscopic space map

The macroscopic balance equations can be obtained from the corresponding mesoscopic ones by simple integration over the unit sphere $\mathfrak{S}^2$. For instance, integrating the equation (3.15) in its partial derivative form (see in Appendix B-2 the balance equations in terms of partial derivatives), one obtains

$$\frac{\partial}{\partial t}\int_{\mathfrak{S}^2} \rho\boldsymbol{v}\, d^2\boldsymbol{n} + \int_{\mathfrak{S}^2} \operatorname{div}(\rho\boldsymbol{v}\otimes\boldsymbol{v} - \boldsymbol{T})\, d^2\boldsymbol{n} + \int_{\mathfrak{S}^2} \nabla_{\boldsymbol{n}}\cdot(\rho\boldsymbol{v}\otimes\boldsymbol{w} - \boldsymbol{T}^*)\, d^2\boldsymbol{n} - \int_{\mathfrak{S}^2} \rho\boldsymbol{f}\, d^2\boldsymbol{n} =$$
$$\frac{\partial}{\partial t}\rho(\boldsymbol{x},t)\boldsymbol{v}(\boldsymbol{x},t) + \operatorname{div}\left[\rho(\boldsymbol{x},t)\boldsymbol{v}(\boldsymbol{x},t)\otimes\boldsymbol{v}(\boldsymbol{x},t) - \boldsymbol{T}(\boldsymbol{x},t)\right] - \rho(\boldsymbol{x},t)\boldsymbol{f}(\boldsymbol{x},t), \tag{3.23}$$

taking into account that the integral over the divergence with respect to the mesoscopic variables vanishes [62], that is,

$$\int_{\mathfrak{S}^2} \nabla_{\boldsymbol{n}}\cdot(\ldots)\, d^2\boldsymbol{n} = 0. \tag{3.24}$$

Hence, the following macroscopic definitions from the mesoscopic quantities are obtained:

- For the linear momentum density,

$$\rho(\boldsymbol{x},t)\boldsymbol{v}(\boldsymbol{x},t)=\int_{\mathfrak{S}^2}\rho\boldsymbol{v}\,d^2\boldsymbol{n}, \tag{3.25}$$

  where according to (3.6) one has

$$\boldsymbol{v}(\boldsymbol{x},t)=\int_{\mathfrak{S}^2}f\boldsymbol{v}\,d^2\boldsymbol{n}. \tag{3.26}$$

- For the stress tensor,

$$\boldsymbol{T}(\boldsymbol{x},t)=\int_{\mathfrak{S}^2}\left[\boldsymbol{T}-\rho\boldsymbol{v}\otimes\boldsymbol{v}\right]\,d^2\boldsymbol{n}+\rho(\boldsymbol{x},t)\boldsymbol{v}(\boldsymbol{x},t)\otimes\boldsymbol{v}(\boldsymbol{x},t). \tag{3.27}$$

- For the momentum supply density

$$\rho(\boldsymbol{x},t)\boldsymbol{f}(\boldsymbol{x},t)=\int_{\mathfrak{S}^2}\rho\boldsymbol{f}\,d^2\boldsymbol{n}. \tag{3.28}$$

In the same way, by integrating the remaining balances, one obtains the mesoscopic definitions of the macroscopic spin $\boldsymbol{s}(\boldsymbol{x},t)$, coupled stress $\boldsymbol{W}(\boldsymbol{x},t)$, specific external angular momentum on spin $\boldsymbol{g}(\boldsymbol{x},t)$, and specific energy $\varepsilon(\boldsymbol{x},t)$,

$$\begin{aligned}
\rho(\boldsymbol{x},t)\boldsymbol{s}(\boldsymbol{x},t)&=\int_{\mathfrak{S}^2}\rho\boldsymbol{s}\,d^2\boldsymbol{n},\\
\boldsymbol{W}(\boldsymbol{x},t)&=\int_{\mathfrak{S}^2}\left[\boldsymbol{W}-\rho\boldsymbol{s}\otimes\boldsymbol{v}\right]\,d^2\boldsymbol{n}+\rho(\boldsymbol{x},t)\boldsymbol{s}(\boldsymbol{x},t)\otimes\boldsymbol{v}(\boldsymbol{x},t),\\
\rho(\boldsymbol{x},t)\boldsymbol{g}(\boldsymbol{x},t)&=\int_{\mathfrak{S}^2}\left[\rho\boldsymbol{g}+\boldsymbol{t}\right]\,d^2\boldsymbol{n}-\boldsymbol{t}(\boldsymbol{x},t),\\
\varepsilon(\boldsymbol{x},t)&=\varepsilon+\frac{1}{2}\left[\boldsymbol{v}^2-\boldsymbol{v}^2(\boldsymbol{x},t)+\boldsymbol{\omega}^2-\boldsymbol{\omega}^2(\boldsymbol{x},t)\right].
\end{aligned} \tag{3.29}$$

Similar relations can be also derived for the heat flux $\boldsymbol{\phi}(\boldsymbol{x},t)$ and the supply $\rho(\boldsymbol{x},t)r(\boldsymbol{x},t)$ terms. One may note that, for constitutive quantities (stress tensor, coupled stress, and etc.), in general the macroscopic quantities are not simply averages of the corresponding mesoscopic ones. Thus, the mesoscopic background can give information, which

is not accessible from the purely macroscopic theory.

Chapter 4

Mesoscopic entropy principle and its consequences

The balance equations for mass, linear momentum, angular momentum and spin, energy, and entropy represent laws that encompass all material behaviors, *i.e.* they hold for any material body regardless of its constitution. However, it is obvious that individual materials such as water and coffee, or hydrogen and oxygen react differently to the same set of physical laws. Hence, the balance laws are not sufficient for determining the various field variables that can appear during the investigation of a particular material. Thus, one must also consider the existence of other more specific laws, which aim to describe different material properties that apparently separate the various materials from one another. Such laws are the so-called material or constitutive equations.[1] These equations are based on fundamental principles and thermodynamic restrictions deduced from the entropy inequality, and they depend on the nature and range of the physical effects desired.

The main reason for postulating the constitutive equations is to attain a closed set of equations such that the field variables can be uniquely determined. This set consists of the balance equations and a number of material equations that make up an ensemble of differential equations, called the field equations. Every solution of the field equations set is considered as a thermodynamic process. In general, such solutions are par-

[1] In this work, one considers two kinds of constitutive variables: the independent constitutive variables, also called state space ones, and dependent constitutive variables. The latter ones depend on the state space variables by imposing the constitutive equations. Note that the constitutive equations themselves are not expressed, but only the sets of independent and dependent constitutive variables.

ticularized through initial and boundary conditions for certain experimental conditions, since the material equations themselves are based on experimental observations.

In the present chapter, the mesoscopic entropy inequality for the mixture under study is evaluated for two sets of constitutive equations only. It is possible to choose among a great number of constitutive equations containing few or many variables. However, depending on the choice of these variables, one can obtain, or not, a physically plausible solution. So, one must be very cautious in selecting material equations and good judgment in choosing them is essential. Therefore, the variables taken into account here are chosen based mainly on experimental observations [1, 43, 44, 46, 47, 48], and in recent studies [52, 54, 64, 65, 66] about mixture theory in continuum and mesoscopic thermodynamics. The first constitutive class involves variables defined in the $\mathbb{R}^3$ manifold only, whilst the second class includes variables defined in both $\mathbb{R}^3$ and the unit sphere $\mathfrak{S}^2$ manifolds. These two classes of constitutive equations are used as prototypes to evaluate the application of the presented theory as well as to help in the determination of the best set of constitutive variables for the mixture under study.

The most simple form of a mixture theory that is capable of describing the dispersion of a number of tracers in a fluid is considered in both prototypes. In this approach, the mixture is assumed to be diluted, such that the main fluid (usually water) is more dominant than all other constituents. In addition, one also assumes an unique temperature field as well as the energy balance equation only for the whole solution[2]. Thus, under these conditions, the thermodynamics of the mixture can be described as that of the main fluid.

4.1 Prototype 1: variables defined in the $\mathbb{R}^3$ manifold

The material objectivity principle requires that constitutive quantities must not depend on the observer, thereby, constitutive functions do not explicitly depend on the velocity, and they depend on the velocity gradient only through its symmetric part, the stretching tensor $\boldsymbol{D}$ [1]. Then, as a consequence, one proposes the following state space,

[2] In plasma modeling, the constituents experience individual temperatures on time scales comparable to transport process times, hence separate energy balances are necessary and, in general, the individual species have different temperatures [64].

$$\Xi \in \{\rho, c_\alpha, \mathrm{grad}(c_\beta), \boldsymbol{D}, \boldsymbol{\omega}, \mathrm{grad}(\boldsymbol{\omega}), \theta, \mathrm{grad}(\theta)\}\,, \quad (\forall \alpha, \beta = 1, ..., N), \tag{4.1}$$

where θ is the empirical temperature. Incidentally, the dependent field quantities,

$$d \in \{\boldsymbol{j}_\alpha, \chi_\alpha, \varepsilon, s, \phi, \boldsymbol{T}, \boldsymbol{W}, \boldsymbol{\mathfrak{E}}\}\,, \tag{4.2}$$

must be formulated as functions on the state space (4.1). Note that all these equations have variables defined only in $\mathbb{R}^3$.

In addition, $\boldsymbol{\omega}$ is also a non-objective quantity, but by using a linear map (duality map) one can establish a one-to-one correspondence between a skew-symmetric objective tensor and a non-objective vector. That is, the dependence of the constitutive functions on $\boldsymbol{\omega}$ occurs by means of a skew-symmetric tensor of type $\boldsymbol{A}_{ij} = e_{ijk}\omega_k$. Thus, with these assumptions, (4.1) becomes

$$\Xi \in \{\rho, c_\alpha, \mathrm{grad}(c_\beta), \boldsymbol{D}, \boldsymbol{A}, \mathrm{grad}(\boldsymbol{\omega}), \theta, \mathrm{grad}(\theta)\}\,, \quad (\forall \alpha, \beta = 1, ..., N), \tag{4.3}$$

where the constitutive quantities are assumed to depend on them,

$$d = d\,\{\Xi\}\,. \tag{4.4}$$

The set of equations (4.4) is analogous to that used in classical continuum mechanics, as can be noted in references [64, 65, 66].

Once all relevant constitutive assumptions and balance equations have been established, the entropy principle can be exploited. For any process of the investigated mixture, the mesoscopic entropy inequality (3.22) must be satisfied subject to the simultaneous satisfaction of the balance laws (3.11), (3.13), (3.15), (3.18) and (3.20). In order to create a link between the entropy balance and the remaining balances, the method of Lagrange multipliers proposed by Liu [45, 47] and proven in [67] is employed. According to this approach, the product of each balance equation with its corresponding Lagrange multiplier is subtracted from the entropy inequality, so that this inequality can be satisfied for unrestricted independent fields [1]. Thus, for the mixture investi-

gated, the extended mesoscopic entropy inequality is given by

$$\rho\frac{ds}{dt}+\operatorname{div}(\mathfrak{E})+\nabla_{\boldsymbol{n}}\cdot(\mathfrak{E}^{*})-\rho\eta-\Lambda^{\rho}\left[\frac{d\rho}{dt}+\rho\operatorname{div}(\boldsymbol{v})+\rho\,\nabla_{\boldsymbol{n}}\cdot(\boldsymbol{w})\right]$$
$$-\sum_{\alpha=1}^{N-1}\Lambda^{c_\alpha}\left[\rho\frac{dc_\alpha}{dt}+\operatorname{div}(\boldsymbol{j}_\alpha)+\nabla_{\boldsymbol{n}}\cdot(\boldsymbol{h}_\alpha)-\chi_\alpha\right]-\Lambda^{\boldsymbol{v}}\cdot\left[\rho\frac{d\boldsymbol{v}}{dt}-\operatorname{div}(\boldsymbol{T})-\nabla_{\boldsymbol{n}}\cdot(\boldsymbol{T}^{*})-\rho\boldsymbol{f}\right]$$
$$-\Lambda^{\boldsymbol{\omega}}\cdot\left[\rho\boldsymbol{I}\frac{d\boldsymbol{\omega}}{dt}-\operatorname{div}(\boldsymbol{W})-\nabla_{\boldsymbol{n}}\cdot(\boldsymbol{W}^{*})-\boldsymbol{t}-\rho\boldsymbol{g}\right]$$
$$-\Lambda^{\varepsilon}\Big[\rho\frac{d\varepsilon}{dt}+\operatorname{div}(\boldsymbol{\phi})+\nabla_{\boldsymbol{n}}\cdot(\boldsymbol{\phi}^{*})-\boldsymbol{T}^{T}:\operatorname{grad}(\boldsymbol{v})-\boldsymbol{W}^{T}:\operatorname{grad}(\boldsymbol{\omega})-\left(\boldsymbol{T}^{*}\right)^{T}:\nabla(\boldsymbol{v})$$
$$-\left(\boldsymbol{W}^{*}\right)^{T}:\nabla(\boldsymbol{\omega})-\boldsymbol{\omega}\cdot\boldsymbol{t}-\rho r\Big]\geq 0. \tag{4.5}$$

Here, $\Lambda^{\rho},\Lambda^{c_\alpha},\Lambda^{\boldsymbol{v}},\Lambda^{\boldsymbol{\omega}},\Lambda^{\varepsilon}$ are Lagrange multipliers of mass, concentration, velocity, angular velocity and energy, respectively. These parameters are auxiliary constitutive quantities that must be determined along with the exploitation of the inequality (4.5). The dot placed after $\Lambda^{\boldsymbol{v}}$ and $\Lambda^{\boldsymbol{\omega}}$ is to be understood as indicating scalar product in $\mathcal{M}^{6}$.

Substituting the constitutive relations (4.4) in (4.5) and performing all required differentiations according to the chain rule of differentiation, one obtains after lengthy manipulations a compact expression of the form

$$\gamma(\Xi)\cdot\sigma+\mathfrak{D}(\Xi)\geq 0, \tag{4.6}$$

where $\gamma(\Xi)$ and $\mathfrak{D}(\Xi)$ are functions of the variables (Ξ) listed in (4.3), and σ represents higher derivatives according to

$$\sigma\in\Big\{\frac{d\rho}{dt},\frac{d}{dt}\operatorname{grad}(\rho),\frac{dc_\alpha}{dt},\frac{d}{dt}\operatorname{grad}(c_\beta),\frac{d\theta}{dt},\frac{d}{dt}\operatorname{grad}(\theta),\frac{d\boldsymbol{A}}{dt},\frac{d\boldsymbol{D}}{dt},\frac{d\boldsymbol{v}}{dt},\frac{d\boldsymbol{\omega}}{dt},\frac{d}{dt}\operatorname{grad}(\boldsymbol{\omega}),$$
$$\operatorname{grad}(\rho),\operatorname{grad}(\theta)^{+},\operatorname{grad}(c_\alpha)^{+},\operatorname{grad}(\boldsymbol{\omega})^{+},\operatorname{grad}(\boldsymbol{D}),\operatorname{grad}(\boldsymbol{A}),$$
$$\nabla(\rho),\nabla[\nabla(c_\beta)],\nabla(\boldsymbol{D}),\nabla[\nabla(\boldsymbol{\omega})],\nabla(\boldsymbol{A}),\nabla[\nabla(\theta)]\Big\}. \tag{4.7}$$

In this set, the symbol $+$ indicates a second operation on the operator gradient in $\mathbb{R}^3$, e.g. $\operatorname{grad}(\rho)^{+}=\operatorname{grad}[\operatorname{grad}(\rho)]$. Hence, by the principle of local solvability [47], the inequality (4.6) must hold for arbitrary values of Ξ and σ [67]. The necessary and

sufficient condition for this is

$$\gamma(\Xi) = 0, \quad \text{and} \quad \mathfrak{D}(\Xi) \geq 0. \tag{4.8}$$

The equations $\gamma(\Xi) = 0$ are frequently called the Liu equations, whereas $\mathfrak{D}(\Xi) \geq 0$ is named the residual entropy inequality. Explicitly, the Liu equations in $\mathcal{M}^6$ are

$$\begin{gathered}
\rho\frac{\partial s}{\partial \rho} - \Lambda^{\rho} - \Lambda^{\varepsilon}\rho\frac{\partial \varepsilon}{\partial \rho} = 0, \\
\rho\frac{\partial s}{\partial c_{\alpha}} - \rho\Lambda^{c_{\alpha}} - \Lambda^{\varepsilon}\rho\frac{\partial \varepsilon}{\partial c_{\alpha}} = 0, \\
\rho\frac{\partial s}{\partial \theta} - \Lambda^{\varepsilon}\rho\frac{\partial \varepsilon}{\partial \theta} = 0, \\
\rho\frac{\partial s}{\partial \operatorname{grad}(c_{\beta})} - \Lambda^{\varepsilon}\rho\frac{\partial \varepsilon}{\partial \operatorname{grad}(c_{\beta})} = 0, \\
\rho\frac{\partial s}{\partial \boldsymbol{D}} - \Lambda^{\varepsilon}\rho\frac{\partial \varepsilon}{\partial \boldsymbol{D}} = 0, \\
\rho\frac{\partial s}{\partial \boldsymbol{A}} - \Lambda^{\varepsilon}\rho\frac{\partial \varepsilon}{\partial \boldsymbol{A}} = 0, \\
\rho\frac{\partial s}{\partial \operatorname{grad}(\boldsymbol{\omega})} - \Lambda^{\varepsilon}\rho\frac{\partial \varepsilon}{\partial \operatorname{grad}(\boldsymbol{\omega})} = 0, \\
\rho\frac{\partial s}{\partial \operatorname{grad}(\theta)} - \Lambda^{\varepsilon}\rho\frac{\partial \varepsilon}{\partial \operatorname{grad}(\theta)} = 0, \\
\rho\frac{\partial s}{\partial \operatorname{grad}(\rho)} - \Lambda^{\varepsilon}\rho\frac{\partial \varepsilon}{\partial \operatorname{grad}(\rho)} = 0, \\
-\rho\Lambda^{\boldsymbol{v}} = 0, \\
-\rho\boldsymbol{I}\Lambda^{\omega} = 0,
\end{gathered} \tag{4.9}$$

$$
\begin{gathered}
\frac{\partial \mathfrak{E}}{\partial \rho}-\sum_{\alpha=1}^{N-1} \Lambda^{c_\alpha} \frac{\partial \boldsymbol{j}_\alpha}{\partial \rho}+\Lambda^{\boldsymbol{v}} \cdot \frac{\partial \boldsymbol{T}}{\partial \rho}+\Lambda^{\boldsymbol{\omega}} \cdot \frac{\partial \boldsymbol{W}}{\partial \rho}-\Lambda^{\varepsilon} \frac{\partial \boldsymbol{\phi}}{\partial \rho}=0, \\
\frac{\partial \mathfrak{E}}{\partial \boldsymbol{D}}-\sum_{\alpha=1}^{N-1} \Lambda^{c_\alpha} \frac{\partial \boldsymbol{j}_\alpha}{\partial \boldsymbol{D}}+\Lambda^{\boldsymbol{v}} \cdot \frac{\partial \boldsymbol{T}}{\partial \boldsymbol{D}}+\Lambda^{\boldsymbol{\omega}} \cdot \frac{\partial \boldsymbol{W}}{\partial \boldsymbol{D}}-\Lambda^{\varepsilon} \frac{\partial \boldsymbol{\phi}}{\partial \boldsymbol{D}}=0, \\
\frac{\partial \mathfrak{E}}{\partial \boldsymbol{A}}-\sum_{\alpha=1}^{N-1} \Lambda^{c_\alpha} \frac{\partial \boldsymbol{j}_\alpha}{\partial \boldsymbol{A}}+\Lambda^{\boldsymbol{v}} \cdot \frac{\partial \boldsymbol{T}}{\partial \boldsymbol{A}}+\Lambda^{\boldsymbol{\omega}} \cdot \frac{\partial \boldsymbol{W}}{\partial \boldsymbol{A}}-\Lambda^{\varepsilon} \frac{\partial \boldsymbol{\phi}}{\partial \boldsymbol{A}}=0, \\
\frac{\partial \mathfrak{E}}{\partial \operatorname{grad}(c_\beta)}-\sum_{\alpha=1}^{N-1} \Lambda^{c_\alpha} \left.\frac{\partial \boldsymbol{j}_\alpha}{\partial \operatorname{grad}(c_\beta)}\right|_{\alpha \neq \beta}+\Lambda^{\boldsymbol{v}} \cdot \frac{\partial \boldsymbol{T}}{\partial \operatorname{grad}(c_\beta)}+\Lambda^{\boldsymbol{\omega}} \cdot \frac{\partial \boldsymbol{W}}{\partial \operatorname{grad}(c_\beta)}-\Lambda^{\varepsilon} \frac{\partial \boldsymbol{\phi}}{\partial \operatorname{grad}(c_\beta)}=0, \\
\frac{\partial \mathfrak{E}}{\partial \operatorname{grad}(\theta)}-\sum_{\alpha=1}^{N-1} \Lambda^{c_\alpha} \frac{\partial \boldsymbol{j}_\alpha}{\partial \operatorname{grad}(\theta)}+\Lambda^{\boldsymbol{v}} \cdot \frac{\partial \boldsymbol{T}}{\partial \operatorname{grad}(\theta)}+\Lambda^{\boldsymbol{\omega}} \cdot \frac{\partial \boldsymbol{W}}{\partial \operatorname{grad}(\theta)}-\Lambda^{\varepsilon} \frac{\partial \boldsymbol{\phi}}{\partial \operatorname{grad}(\theta)}=0, \\
\frac{\partial \mathfrak{E}}{\partial \operatorname{grad}(\boldsymbol{\omega})}-\sum_{\alpha=1}^{N-1} \Lambda^{c_\alpha} \frac{\partial \boldsymbol{j}_\alpha}{\partial \operatorname{grad}(\boldsymbol{\omega})}+\Lambda^{\boldsymbol{v}} \cdot \frac{\partial \boldsymbol{T}}{\partial \operatorname{grad}(\boldsymbol{\omega})}+\Lambda^{\boldsymbol{\omega}} \cdot \frac{\partial \boldsymbol{W}}{\partial \operatorname{grad}(\boldsymbol{\omega})}-\Lambda^{\varepsilon} \frac{\partial \boldsymbol{\phi}}{\partial \operatorname{grad}(\boldsymbol{\omega})}=0,
\end{gathered}
\tag{4.10}
$$

and from the inequality $(4.8)_2$ one finds the mesoscopic residual entropy production as the state space function

$$
\begin{aligned}
\mathfrak{D}=&\left[\frac{\partial \mathfrak{E}}{\partial c_\beta}-\sum_{\alpha=1}^{N-1} \Lambda^{c_\alpha} \frac{\partial \boldsymbol{j}_\alpha}{\partial c_\beta}-\Lambda^{\varepsilon} \frac{\partial \boldsymbol{\phi}}{\partial c_\beta}\right] \cdot \operatorname{grad}(c_\beta)+\left[\frac{\partial \mathfrak{E}}{\partial \theta}-\sum_{\alpha=1}^{N-1} \Lambda^{c_\alpha} \frac{\partial \boldsymbol{j}_\alpha}{\partial \theta}-\Lambda^{\varepsilon} \frac{\partial \boldsymbol{\phi}}{\partial \theta}\right] \cdot \operatorname{grad}(\theta) \\
&-\rho \Lambda^{\rho} \boldsymbol{1}: \boldsymbol{D}-\rho \Lambda^{\rho} \nabla_{\boldsymbol{n}} \cdot(\boldsymbol{w})-\sum_{\alpha=1}^{N-1} \Lambda^{c_\alpha} \nabla_{\boldsymbol{n}} \cdot\left(\boldsymbol{h}_\alpha\right)+\Lambda^{\varepsilon} \boldsymbol{T}: \boldsymbol{D}+\Lambda^{\varepsilon} \boldsymbol{W}^T: \operatorname{grad}(\boldsymbol{\omega}) \\
&-\Lambda^{\varepsilon}\left(\boldsymbol{T}^*\right)^T: \nabla(\boldsymbol{v})+\Lambda^{\varepsilon}\left(\boldsymbol{W}^*\right)^T: \nabla(\boldsymbol{\omega})+\Lambda^{\varepsilon} \boldsymbol{\omega} \cdot \boldsymbol{t}+\sum_{\alpha=1}^{N-1} \Lambda^{c_\alpha} \chi_\alpha \geq 0.
\end{aligned}
\tag{4.11}
$$

Note that terms containing the Lagrange multipliers of velocity $\Lambda^{\boldsymbol{v}}$ and angular velocity $\Lambda^{\boldsymbol{\omega}}$ do not appear in the above equation. This is due to Liu equations $(4.9)_{10,11}$, which require that such multipliers are zero, since neither the density nor the inertia momentum tensor can be null.

Our next goal is to draw inferences from these mathematical expressions.

4.1.1 Comparison to Classical Thermodynamics

First of all, the Lagrange multiplier of energy is assumed a function of the empirical temperature θ only, that is, $\Lambda^{\varepsilon}=\Lambda^{\varepsilon}(\theta)$. This assumption is justified in Müller's book [46]

and in recent papers [64, 65] about mixture theory. So, once this assumption is taken into account, by cross-differentiation one obtains from $(4.9)_{3,5}$ that

$$\frac{\partial^2 s}{\partial \boldsymbol{D}\partial\theta} - \Lambda^{\varepsilon}\frac{\partial^2 \varepsilon}{\partial \boldsymbol{D}\partial\theta} = \frac{\partial^2 s}{\partial\theta\partial \boldsymbol{D}} - \Lambda^{\varepsilon}\frac{\partial^2 \varepsilon}{\partial\theta\partial \boldsymbol{D}} - \left(\frac{\partial \Lambda^{\varepsilon}}{\partial\theta}\right)\left(\frac{\partial \varepsilon}{\partial \boldsymbol{D}}\right), \tag{4.12}$$

from which one concludes that $\partial\varepsilon/\partial\boldsymbol{D} = 0$, since $\partial\Lambda^{\varepsilon}/\partial\theta \neq 0$. In view of $(4.9)_5$, one also abtains $\partial\, s/\partial\boldsymbol{D} = 0$. Thus, the internal energy and entropy cannot depend on $\boldsymbol{D}$. Likewise, by using $(4.9)_{3,4,6,7,8,9}$ one may show that s and ε can neither depend on $\mathrm{grad}(c_\beta)$, $\boldsymbol{A}$, $\mathrm{grad}(\boldsymbol{\omega})$, and $\mathrm{grad}(\theta)$. Hence, the identities $(4.9)_{1,2,3,5,4,6,7,8,9}$ are reduced to the following statements

$$\begin{aligned}
\frac{\partial s}{\partial\theta} &= \Lambda^{\varepsilon}\frac{\partial\varepsilon}{\partial\theta},\\
\frac{\partial s}{\partial\rho} = \frac{1}{\rho}\Lambda^{\rho} + \Lambda^{\varepsilon}\frac{\partial\varepsilon}{\partial\rho} &= \Lambda^{\varepsilon}\left(\frac{\partial\varepsilon}{\partial\rho} - \frac{p}{\rho^2}\right), \qquad p := -\frac{\Lambda^{\rho}}{\Lambda^{\varepsilon}}\rho,\\
\frac{\partial s}{\partial c_\alpha} = \Lambda^{\varepsilon}\frac{\partial\varepsilon}{\partial c_\alpha} + \Lambda^{c_\alpha} &= \Lambda^{\varepsilon}\left(\frac{\partial\varepsilon}{\partial c_\alpha} - \mu_\alpha\right), \qquad \mu_\alpha := -\frac{\Lambda^{c_\alpha}}{\Lambda^{\varepsilon}},
\end{aligned} \tag{4.13}$$

where $\Lambda^{\varepsilon} = \Lambda^{\varepsilon}(\theta)$, $\Lambda^{\rho} = \Lambda^{\rho}(\rho, c_\alpha, \theta)$, $\Lambda^{c_\alpha} = \Lambda^{c_\alpha}(\rho, c_\alpha, \theta)$, $s = s(\rho, c_\alpha, \theta)$ and $\varepsilon = \varepsilon(\rho, c_\alpha, \theta)$.

Starting from (4.13) one may obtain the total differential of the mesoscopic entropy,

$$\begin{aligned}
ds = \Lambda^{\varepsilon}\left[\frac{\partial\varepsilon}{\partial\theta}d\theta + \left(\frac{\partial\varepsilon}{\partial\rho} + \frac{\Lambda^{\rho}}{\Lambda^{\varepsilon}}\frac{1}{\rho}\right)d\rho + \sum_{\alpha=1}^{N-1}\left(\frac{\partial\varepsilon}{\partial c_\alpha} + \frac{\Lambda^{c_\alpha}}{\Lambda^{\varepsilon}}\right)dc_\alpha\right], \text{ or}\\
ds = \Lambda^{\varepsilon}\left[d\varepsilon - p\left(\frac{1}{\rho^2}\right)d\rho - \sum_{\alpha=1}^{N-1}\mu_\alpha dc_\alpha\right].
\end{aligned} \tag{4.14}$$

This equation is similar to the so-called Gibbs relation in macroscopic continuum thermodynamics, which connects the total differential of the entropy with the absolute temperature Θ. Thereby, by comparing the equations, one can deduce from (4.14) that $\Lambda^{\varepsilon}(\theta) = \Theta^{-1}$. It is important to note that the definition of $\Lambda^{\varepsilon}(\theta)$ arises naturally in this text, unlike what is done in references [65, 66], where $\Lambda^{\varepsilon}(\theta) = \Theta^{-1}$ is imposed in advance. In addition, $(4.13)_{2,3}$ also provide definitions for p and μ_α. Such quantities are identified as the thermodynamic pressure and the chemical potential of constituent $\alpha = 1, \ldots, N-1$ in relation to that of constituent $\alpha = N$, respectively [1]. The proof for these latter identifications is given bellow

Proof 4.1 *If the concentrations* $c_\alpha(\alpha = 1, 2, ..., N)$ *for all constituents were used, then instead of (4.14) one would have obtained,*

$$\begin{aligned} ds &= \frac{1}{\Theta}\left[d\varepsilon - p\left(\frac{1}{\rho^2}\right)d\rho - \sum_{\alpha=1}^{N}\bar{\mu}_\alpha dc_\alpha\right] \\ &= \frac{1}{\Theta}\left[d\varepsilon - p\left(\frac{1}{\rho^2}\right)d\rho - \sum_{\alpha=1}^{N-1}\left(\bar{\mu}_\alpha - \bar{\mu}_N\right)dc_\alpha\right], \end{aligned} \tag{4.15}$$

where the relation $\sum_{\alpha=1}^{N} c_\alpha = 1$ *was used. Thus, one necessarily has*

$$\mu_\alpha = \left(\bar{\mu}_\alpha - \bar{\mu}_N\right)\big|_{c_N = 1 - \sum_{\alpha=1}^{N-1} c_\alpha}, \tag{4.16}$$

that is, the variable μ_α *in (4.14) is the difference of the chemical potentials* $(\bar{\mu}_\alpha - \bar{\mu}_N)$*.*

Furthermore, one also obtains the integrability conditions from (4.14) by performing the respective cross differentiations,

$$\frac{\partial \mu_\alpha}{\partial \rho} = \frac{\partial}{\partial c_\alpha}\left(\frac{p}{\rho^2}\right), \qquad \frac{\partial \mu_\alpha}{\partial c_\beta} = \frac{\partial \mu_\beta}{\partial c_\alpha}, \qquad (\forall \alpha, \beta = 1, ..., N-1) \tag{4.17}$$

as well as

$$\frac{d(\ln \Lambda^\varepsilon)}{d\theta} = \frac{1}{\Lambda^\varepsilon}\frac{d\Lambda^\varepsilon}{d\theta} = \frac{\partial \mu_\alpha/\partial\theta}{\partial\varepsilon/\partial c_\alpha - \mu_\alpha} = \frac{\partial p/\partial\theta}{(\partial\varepsilon/\partial\rho)\rho^2 - p}, \ \ (\forall \alpha, \beta = 1, ..., N-1). \tag{4.18}$$

Equation $(4.17)_2$ is the well-known Gibbs-Duhem expression that describes the relationship among the constituent chemical potential changes in a thermodynamic system. Moreover, the equation (4.18) is similar to the one used by Müller [46] to identity the empirical temperature θ with the temperature of ideal gases.

4.1.2 Entropy flux and residual inequality

By regarding equations (4.10), a flux vector $\mathfrak{Y}$ can be defined in $\mathbb{R}^3$ so that

$$\mathfrak{Y} = \mathfrak{E} - \Lambda^\varepsilon \boldsymbol{\phi} - \Lambda^\varepsilon \sum_{\alpha=1}^{N-1} \mu_\alpha \boldsymbol{j}_\alpha. \tag{4.19}$$

Substituting this definition into the corresponding equation (4.10), one has

$$\frac{\partial \mathfrak{Y}}{\partial \rho} = \Lambda^{\varepsilon} \sum_{\alpha=1}^{N-1} \frac{\partial \mu_{\alpha}}{\partial \rho} \boldsymbol{j}_{\alpha}, \qquad \frac{\partial \mathfrak{Y}}{\partial \boldsymbol{D}} = \Lambda^{\varepsilon} \sum_{\alpha=1}^{N-1} \frac{\partial \mu_{\alpha}}{\partial \boldsymbol{D}} \boldsymbol{j}_{\alpha},$$
$$\frac{\partial \mathfrak{Y}}{\partial \boldsymbol{A}} = \Lambda^{\varepsilon} \sum_{\alpha=1}^{N-1} \frac{\partial \mu_{\alpha}}{\partial \boldsymbol{A}} \boldsymbol{j}_{\alpha}, \qquad \frac{\partial \mathfrak{Y}}{\partial \mathrm{grad}(c_{\beta})} = \Lambda^{\varepsilon} \sum_{\alpha=1}^{N-1} \frac{\partial \mu_{\alpha}}{\partial \mathrm{grad}(c_{\beta})} \boldsymbol{j}_{\alpha},$$
$$\frac{\partial \mathfrak{Y}}{\partial \mathrm{grad}(\theta)} = \Lambda^{\varepsilon} \sum_{\alpha=1}^{N-1} \frac{\partial \mu_{\alpha}}{\partial \mathrm{grad}(\theta)} \boldsymbol{j}_{\alpha}, \qquad \frac{\partial \mathfrak{Y}}{\partial \mathrm{grad}(\boldsymbol{\omega})} = \Lambda^{\varepsilon} \sum_{\alpha=1}^{N-1} \frac{\partial \mu_{\alpha}}{\partial \mathrm{grad}(\boldsymbol{\omega})} \boldsymbol{j}_{\alpha}, \tag{4.20}$$

In the above equations, the definition $\mu_{\alpha} = -\Lambda^{c_{\alpha}}/\Lambda^{\varepsilon}$ was used together with the definitions of the Lagrange multipliers $\Lambda^{\boldsymbol{v}} = 0$ and $\Lambda^{\boldsymbol{\omega}} = 0$ arising from $(4.9)_{10,11}$. Note that the reduced dependence of $\Lambda^{c_{\alpha}}$ is reflected in μ_{α}, such that $\mu_{\alpha}(\rho, c_{\alpha}, \theta)$. Then, since the above derivatives must vanish, the vector $\mathfrak{Y}$ is function of the variables ρ, c_{α}, θ only, and a reasonable assumption, which is compatible with the second law of thermodynamics is $\mathfrak{Y} = 0$. This assumption does not implies equilibrium or its vicinity. As a result, the mesoscopic entropy flow vector in $\mathbb{R}^3$ is defined as

$$\mathfrak{E} = \Lambda^{\varepsilon} \boldsymbol{\phi} - \Lambda^{\varepsilon} \sum_{\alpha=1}^{N-1} \mu_{\alpha} \boldsymbol{j}_{\alpha} = \left(\boldsymbol{\phi} - \sum_{\alpha=1}^{N-1} \mu_{\alpha} \boldsymbol{j}_{\alpha} \right) / \Theta. \tag{4.21}$$

This definition implies that the total entropy flux in the mesoscopic space is the sum of a diffusive flux and a heat flux contribution, both defined in $\mathbb{R}^3$. Such an outcome is identical to that obtained in macroscopic continuum thermodynamics [1, 43, 44, 46, 47, 50, 54, 65, 66], where the entropy flux deviates from the heat flux via a vector, which is a linear combination of the diffusive fluxes.

Another form of the mesoscopic residual entropy inequality may be obtained by using (4.21) and (4.11),

$$\mathfrak{D} = \left(\sum_{\alpha=1}^{N-1} \mu_{\alpha} \boldsymbol{j}_{\alpha} - \boldsymbol{\phi} \right) \cdot \frac{\mathrm{grad}(\Theta)}{\Theta} - \sum_{\alpha=1}^{N-1} \boldsymbol{j}_{\alpha} \cdot \mathrm{grd}(\mu_{\alpha}) + (\boldsymbol{T} + p\boldsymbol{1}) \cdot \boldsymbol{D} - \sum_{r=1}^{R} \mathfrak{F}_r \Omega_r$$
$$+ \boldsymbol{W}^T : \mathrm{grad}(\boldsymbol{\omega}) - \rho \Lambda^{\rho} \nabla_{\boldsymbol{n}} \cdot (\boldsymbol{w}) + \sum_{\alpha=1}^{N-1} \mu_{\alpha} \nabla_{\boldsymbol{n}} \cdot (\boldsymbol{h}_{\alpha})$$
$$+ (\boldsymbol{T}^*)^T : \nabla(\boldsymbol{v}) + (\boldsymbol{W}^*)^T : \nabla(\boldsymbol{\omega}) \geq 0, \tag{4.22}$$

where $\boldsymbol{\omega} \cdot \boldsymbol{t} = 0$ according to [65, 66]. In equation (4.22), the definitions $\mu_{\alpha} = -\Lambda^{c_{\alpha}}/\Lambda^{\varepsilon}$

and $\Lambda^{\varepsilon}(\theta) = \Theta^{-1}$ were used. The symbol $\mathrm{grd}(\mu_\alpha)$ denotes the reduced gradient of μ_α, in which the density is regarded as constant, i.e.,

$$\mathrm{grd}(\mu_\alpha) = \sum_{\beta=1}^{N} \frac{\partial \mu_\alpha}{\partial\, c_\beta} \mathrm{grad}(c_\beta) + \frac{\partial \mu_\alpha}{\partial \theta} \mathrm{grad}(\theta). \tag{4.23}$$

Note that in (4.22) the relation between chemical affinity $\mathfrak{F}$ and mass production χ_α was also used , which is given by the following expression,

$$\sum_{\alpha=1}^{N-1} \chi_\alpha \mu_\alpha = \sum_{k=1}^{R} \mathfrak{F}_k \Omega_k. \tag{4.24}$$

Here, $\mathfrak{F}_k$ is the chemical affinity of a reaction k and Ω_k the rate of conversion of k, supposing R independent chemical reactions. Note that μ_α includes the corresponding stoichiometric coefficient. The latter equation (4.24) is in agreement with Bedford and Bowen's works [68, 69, 70]. The next step is to investigate the thermodynamic implications of the mesoscopic residual entropy inequality (4.22) in the equilibrium state.

4.1.3 Thermodynamic restrictions

In mesoscopic space, the thermodynamic equilibrium state will be defined as that whose mesoscopic residual entropy production assumes its minimum value. This definition is the same used to define a equilibrium state in the macroscopic space. However, in passing it can be noted that there is a preconceived opinion stating that at equilibrium all quantities are time independent and there are no gradients. It turns out this concept is wrong, as the following simple example demonstrates: if there is a gravitational field, one also has a gradient of mass density at equilibrium, and if an observer is freely falling in this gravitational field, he (she) realizes that the mass density is changing in time although the system is at equilibrium. Consequently, time independence and vanishing gradients cannot be used as equilibrium conditions [4]. Thus, in this work, one imposes that (4.22) must satisfy the weaker conditions

$$\left.\frac{\partial \mathfrak{D}}{\partial \xi}\right|_E = 0, \qquad \left.\left(\frac{\partial^2 \mathfrak{D}}{\partial \xi^2}\right)\right|_E \geq 0, \tag{4.25}$$

where, $\xi \in \{\Omega_k, \boldsymbol{D}, \mathrm{grad}(\Theta), \mathrm{grad}(\boldsymbol{\omega}), \mathrm{grd}(\mu_\alpha), \nabla(\boldsymbol{v}), \nabla(\boldsymbol{\omega}), \nabla_{\boldsymbol{n}} \cdot (\boldsymbol{w}), \nabla_{\boldsymbol{n}} \cdot (\boldsymbol{h}_\alpha)\}$ is the set of variables in (4.22). The index E stands for the local equilibrium state.

In order to evaluate the validity of the prototype presented here, the following proposition is used:

Proposition 4.1 *If (4.25)$_1$ produces physically inconsistent results at equilibrium, then, a prototype with material equations defined in (4.2) and (4.3) is not suitable to describe the behavior of the proposed solution.*

Thereafter, from inequality (4.22) and equation (4.25)$_1$, at local equilibrium the first-order derivatives of the residual mesoscopic entropy production can be given by

$$\left.\frac{\partial \mathfrak{D}}{\partial\, \mathrm{grad}(\mu_\alpha)}\right|_E = -\boldsymbol{j}_\alpha = 0, \quad (\forall \alpha = 1, ..., N-1), \tag{4.26}$$

$$\left.\frac{\partial \mathfrak{D}}{\partial\, \mathrm{grad}(\Theta)}\right|_E = \frac{1}{\Theta}\left(\sum_{\alpha=1}^{N-1} \mu_\alpha \boldsymbol{j}_\alpha - \boldsymbol{\phi}\right) = 0, \tag{4.27}$$

or yet

$$\left.\frac{\partial \mathfrak{D}}{\partial\, \mathrm{grad}(\Theta)}\right|_E = \frac{\boldsymbol{\phi}}{\Theta} = 0,$$

$$\left.\frac{\partial \mathfrak{D}}{\partial\, \mathrm{grad}(\boldsymbol{\omega})}\right|_E = \boldsymbol{W}^T = 0, \tag{4.28}$$

$$\left.\frac{\partial \mathfrak{D}}{\partial \nabla(\boldsymbol{\omega})}\right|_E = (\boldsymbol{W}^*)^T = 0, \tag{4.29}$$

$$\left.\frac{\partial \mathfrak{D}}{\partial \nabla(\boldsymbol{v})}\right|_E = (\boldsymbol{T}^*)^T = 0, \tag{4.30}$$

$$\left.\frac{\partial \mathfrak{D}}{\partial \nabla_{\boldsymbol{n}} \cdot (\boldsymbol{h}_\alpha)}\right|_E = \sum_{\alpha=1}^{N-1} \mu_\alpha = 0, \tag{4.31}$$

$$\left.\frac{\partial \mathfrak{D}}{\partial \boldsymbol{D}}\right|_E = \boldsymbol{T} + p\boldsymbol{1} = 0, \tag{4.32}$$

that produces

$$\left.\boldsymbol{T}\right|_E = -p\boldsymbol{1},$$

and

$$\left.\frac{\partial \mathfrak{D}}{\partial\, \Omega_k}\right|_E = -\mathfrak{F}_k = 0, \quad (\forall k = 1, ..., R). \tag{4.33}$$

The above results are in agreement with recent works in continuum thermodynamics [52, 54, 64, 65, 66] and with experimental observations [1, 43, 44, 46, 47, 48]. However, the derivative

$$\left.\frac{\partial \mathfrak{D}}{\partial \nabla_{\boldsymbol{n}} \cdot (\boldsymbol{w})}\right|_E = \rho\Lambda^\rho = 0, \tag{4.34}$$

show the physically inconsistent result $\Lambda^\rho = 0$. This result is also inconsistent with equation $(4.13)_2$ derived for this prototype. Therefore, in view of these findings and of proposition (4.1), one concludes that the material equations defined in (4.2) and (4.3) are not suitable to describe the behavior of the mixture under study. Hence, it is necessary to develop a new prototype with a new set of constitutive equations. This will be done in the next section.

As a final comment, it is worth mentioning that, even though the material equations (4.2) and (4.3) are not adequate, nevertheless, some classical equations of thermodynamics were obtained. This shows that, when a thermodynamic approach provides consistent results with those of classical thermodynamics, such findings do not represent any guarantee that the considered approach is valid. As a matter of fact, compa-

rable findings must be considered as only a necessary condition, but not sufficient one for a thermodynamic approach to be considered correct.

4.2 Prototype 2: variables defined in $\mathbb{R}^3$ and $\mathfrak{S}^2$

As prototype 1 presented some incoherent theoretical and experimental results, then, in this section a new prototype is proposed with variables defined in both the $\mathbb{R}^3$ and $\mathfrak{S}^2$ manifolds. A set of independent constitutive variables similar to (4.3) is considered. But, now, the mesoscopic change velocity $\boldsymbol{w}$ of the microscopic director $\boldsymbol{n}$, which is a variable defined in $\mathfrak{S}^2$, is added. Hence, the state space is

$$\mathscr{Y} \in \{\rho, c_\alpha, \mathrm{grad}(c_\beta), \boldsymbol{w}, \boldsymbol{D}, \boldsymbol{A}, \mathrm{grad}(\boldsymbol{\omega}), \theta, \mathrm{grad}(\theta)\}, \quad (\forall \alpha, \beta = 1, ..., N). \tag{4.35}$$

Incidentally, the dependent constitutive quantities are given by

$$\mathscr{D} \in \{\boldsymbol{j}_\alpha, \boldsymbol{h}_\alpha, \chi_\alpha, \varepsilon, s, \boldsymbol{\phi}, \boldsymbol{\phi}^*, \boldsymbol{T}, \boldsymbol{T}^*, \boldsymbol{W}, \boldsymbol{W}^*, \boldsymbol{\mathfrak{E}}, \boldsymbol{\mathfrak{E}}^*\}, \tag{4.36}$$

where some variables defined in $\mathfrak{S}^2$ such as the rotational diffusive flux $\boldsymbol{h}_\alpha$, heat flux $\boldsymbol{\phi}^*$, stress tensor $\boldsymbol{T}^*$, couple tensor $\boldsymbol{W}^*$ and entropy flux vector $\boldsymbol{\mathfrak{E}}^*$, are added. Note that these material equations are much more complex than those used in prototype 1. Thus, henceforward one assumes the proposition:

Proposition 4.2 *The constitutive equations given by (4.35) and (4.36) define a viscous fluid mixture with conduction of heat, diffusion, and chemical reactions.*

4.2.1 Method of Lagrange multipliers

According to the method of Lagrange multipliers for exploitation of the mesoscopic entropy inequality, there exist the Lagrange multipliers $\Lambda^\rho, \Lambda^{c_\alpha}, \Lambda^{\boldsymbol{v}}, \Lambda^{\boldsymbol{\omega}}, \Lambda^\varepsilon$ that, whenever multiplied by their corresponding balance laws, they produce an inequality,

$$\rho\frac{ds}{dt} + \operatorname{div}(\mathfrak{E}) + \nabla_{\boldsymbol{n}} \cdot (\mathfrak{E}^*) - \rho\eta - \Lambda^{\rho}\left[\frac{d\rho}{dt} + \rho\operatorname{div}(\boldsymbol{v}) + \rho\nabla_{\boldsymbol{n}} \cdot (\boldsymbol{w})\right]$$
$$-\sum_{\alpha=1}^{N-1}\Lambda^{c_\alpha}\left[\rho\frac{dc_\alpha}{dt} + \operatorname{div}(\boldsymbol{j}_\alpha) + \nabla_{\boldsymbol{n}} \cdot (\boldsymbol{h}_\alpha) - \chi_\alpha\right] - \Lambda^{\boldsymbol{v}} \cdot \left[\rho\frac{d\boldsymbol{v}}{dt} - \operatorname{div}(\boldsymbol{T}) - \nabla_{\boldsymbol{n}} \cdot (\boldsymbol{T}^*) - \rho\boldsymbol{f}\right]$$
$$-\Lambda^{\boldsymbol{\omega}} \cdot \left[\rho\boldsymbol{I}\frac{d\boldsymbol{\omega}}{dt} - \operatorname{div}(\boldsymbol{W}) - \nabla_{\boldsymbol{n}} \cdot (\boldsymbol{W}^*) - \boldsymbol{t} - \rho\boldsymbol{g}\right]$$
$$-\Lambda^{\varepsilon}\Big[\rho\frac{d\varepsilon}{dt} + \operatorname{div}(\boldsymbol{\phi}) + \nabla_{\boldsymbol{n}} \cdot (\boldsymbol{\phi}^*) - \boldsymbol{T}^T \cdot \operatorname{grad}(\boldsymbol{v}) - \boldsymbol{W}^T \cdot \operatorname{grad}(\boldsymbol{\omega}) - (\boldsymbol{T}^*)^T : \nabla(\boldsymbol{v})$$
$$-(\boldsymbol{W}^*)^T : \nabla(\boldsymbol{\omega}) - \boldsymbol{\omega} \cdot \boldsymbol{t} - \rho r\Big] \geq 0, \tag{4.37}$$

which must hold for any solution $\{\rho, c_\alpha, \boldsymbol{v}, \boldsymbol{w}, \boldsymbol{\omega}, \theta\}$ of the field equations. Note that the equation (4.37) is similar to (4.5).

After introducing the constitutive equations (4.35) and (4.36) into inequality (4.37) and all differentiations are performed according to the chain rule, then the entropy inequality becomes

$$\frac{d\rho}{dt}\left[\rho\frac{\partial s}{\partial\rho}-\Lambda^{\rho}-\Lambda^{\varepsilon}\rho\frac{\partial\varepsilon}{\partial\rho}\right]+\sum_{\alpha=1}^{N-1}\frac{dc_{\alpha}}{dt}\left[\rho\frac{\partial s}{\partial c_{\alpha}}-\rho\Lambda^{c_{\alpha}}-\Lambda^{\varepsilon}\rho\frac{\partial\varepsilon}{\partial c_{\alpha}}\right]+\frac{d\theta}{dt}\left[\rho\frac{\partial s}{\partial\theta}-\Lambda^{\varepsilon}\rho\frac{\partial\varepsilon}{\partial\theta}\right]+$$

$$\sum_{\alpha=1}^{N-1}\frac{d\,\mathrm{grad}(c_{\beta})}{dt}\cdot\left[\rho\frac{\partial s}{\partial\,\mathrm{grad}(c_{\beta})}-\Lambda^{\varepsilon}\rho\frac{\partial\varepsilon}{\partial\,\mathrm{grad}(c_{\beta})}\right]+\frac{d\boldsymbol{w}}{dt}\cdot\left[\rho\frac{\partial s}{\partial\boldsymbol{w}}-\Lambda^{\varepsilon}\rho\frac{\partial\varepsilon}{\partial\boldsymbol{w}}\right]+$$

$$\frac{d\boldsymbol{D}}{dt}\cdot\left[\rho\frac{\partial s}{\partial\boldsymbol{D}}-\Lambda^{\varepsilon}\rho\frac{\partial\varepsilon}{\partial\boldsymbol{D}}\right]+\frac{d\boldsymbol{A}}{dt}\cdot\left[\rho\frac{\partial s}{\partial\boldsymbol{A}}-\Lambda^{\varepsilon}\rho\frac{\partial\varepsilon}{\partial\boldsymbol{A}}\right]+\frac{d\,\mathrm{grad}(\boldsymbol{\omega})}{dt}\cdot\left[\rho\frac{\partial s}{\partial\,\mathrm{grad}(\boldsymbol{\omega})}-\Lambda^{\varepsilon}\rho\frac{\partial\varepsilon}{\partial\,\mathrm{grad}(\boldsymbol{\omega})}\right]+$$

$$\frac{d\,\mathrm{grad}(\theta)}{dt}\cdot\left[\rho\frac{\partial s}{\partial\,\mathrm{grad}(\theta)}-\Lambda^{\varepsilon}\rho\frac{\partial\varepsilon}{\partial\,\mathrm{grad}(\theta)}\right]+\frac{d\boldsymbol{v}}{dt}\cdot[\rho\Lambda^{\boldsymbol{v}}]+\frac{d\boldsymbol{\omega}}{dt}\cdot[\rho\boldsymbol{I}\Lambda^{\boldsymbol{\omega}}]+$$

$$\mathrm{grad}(\rho)\cdot\left[\frac{\partial\mathfrak{E}}{\partial\rho}-\sum_{\alpha=1}^{N-1}\Lambda^{c_{\alpha}}\frac{\partial\boldsymbol{j}_{\alpha}}{\partial\rho}+\Lambda^{\boldsymbol{v}}\cdot\frac{\partial\boldsymbol{T}}{\partial\rho}+\Lambda^{\boldsymbol{\omega}}\cdot\frac{\partial\boldsymbol{W}}{\partial\rho}-\Lambda^{\varepsilon}\frac{\partial\boldsymbol{\phi}}{\partial\rho}\right]+$$

$$\nabla(\rho)\cdot\left[\frac{\partial\mathfrak{E}^{*}}{\partial\rho}-\sum_{\alpha=1}^{N-1}\Lambda^{c_{\alpha}}\frac{\partial\boldsymbol{h}_{\alpha}}{\partial\rho}+\Lambda^{\boldsymbol{v}}\cdot\frac{\partial\boldsymbol{T}^{*}}{\partial\rho}+\Lambda^{\boldsymbol{\omega}}\cdot\frac{\partial\boldsymbol{W}^{*}}{\partial\rho}-\Lambda^{\varepsilon}\frac{\partial\boldsymbol{\phi}^{*}}{\partial\rho}\right]+$$

$$\mathrm{grad}(\boldsymbol{w})\cdot\left[\frac{\partial\mathfrak{E}}{\partial\boldsymbol{w}}-\sum_{\alpha=1}^{N-1}\Lambda^{c_{\alpha}}\frac{\partial\boldsymbol{j}_{\alpha}}{\partial\boldsymbol{w}}+\Lambda^{\boldsymbol{v}}\cdot\frac{\partial\boldsymbol{T}}{\partial\boldsymbol{w}}+\Lambda^{\boldsymbol{\omega}}\cdot\frac{\partial\boldsymbol{W}}{\partial\boldsymbol{w}}-\Lambda^{\varepsilon}\frac{\partial\boldsymbol{\phi}}{\partial\boldsymbol{w}}\right]+$$

$$\nabla(\boldsymbol{w})\cdot\left[\frac{\partial\mathfrak{E}^{*}}{\partial\boldsymbol{w}}-\sum_{\alpha=1}^{N-1}\Lambda^{c_{\alpha}}\frac{\partial\boldsymbol{h}_{\alpha}}{\partial\boldsymbol{w}}+\Lambda^{\boldsymbol{v}}\cdot\frac{\partial\boldsymbol{T}^{*}}{\partial\boldsymbol{w}}+\Lambda^{\boldsymbol{\omega}}\cdot\frac{\partial\boldsymbol{W}^{*}}{\partial\boldsymbol{w}}-\Lambda^{\varepsilon}\frac{\partial\boldsymbol{\phi}^{*}}{\partial\boldsymbol{w}}\right]+$$

$$\mathrm{grad}(\boldsymbol{D})\cdot\left[\frac{\partial\mathfrak{E}}{\partial\boldsymbol{D}}-\sum_{\alpha=1}^{N-1}\Lambda^{c_{\alpha}}\frac{\partial\boldsymbol{j}_{\alpha}}{\partial\boldsymbol{D}}+\Lambda^{\boldsymbol{v}}\cdot\frac{\partial\boldsymbol{T}}{\partial\boldsymbol{D}}+\Lambda^{\boldsymbol{\omega}}\cdot\frac{\partial\boldsymbol{W}}{\partial\boldsymbol{D}}-\Lambda^{\varepsilon}\frac{\partial\boldsymbol{\phi}}{\partial\boldsymbol{D}}\right]+$$

$$\nabla(\boldsymbol{D})\cdot\left[\frac{\partial\mathfrak{E}^{*}}{\partial\boldsymbol{D}}-\sum_{\alpha=1}^{N-1}\Lambda^{c_{\alpha}}\frac{\partial\boldsymbol{h}_{\alpha}}{\partial\boldsymbol{D}}+\Lambda^{\boldsymbol{v}}\cdot\frac{\partial\boldsymbol{T}^{*}}{\partial\boldsymbol{D}}+\Lambda^{\boldsymbol{\omega}}\cdot\frac{\partial\boldsymbol{W}^{*}}{\partial\boldsymbol{D}}-\Lambda^{\varepsilon}\frac{\partial\boldsymbol{\phi}^{*}}{\partial\boldsymbol{D}}\right]+$$

$$\mathrm{grad}(\boldsymbol{A})\cdot\left[\frac{\partial\mathfrak{E}}{\partial\boldsymbol{A}}-\sum_{\alpha=1}^{N-1}\Lambda^{c_{\alpha}}\frac{\partial\boldsymbol{j}_{\alpha}}{\partial\boldsymbol{A}}+\Lambda^{\boldsymbol{v}}\cdot\frac{\partial\boldsymbol{T}}{\partial\boldsymbol{A}}+\Lambda^{\boldsymbol{\omega}}\cdot\frac{\partial\boldsymbol{W}}{\partial\boldsymbol{A}}-\Lambda^{\varepsilon}\frac{\partial\boldsymbol{\phi}}{\partial\boldsymbol{A}}\right]+$$

$$\nabla(\boldsymbol{A})\cdot\left[\frac{\partial\mathfrak{E}^{*}}{\partial\boldsymbol{A}}-\sum_{\alpha=1}^{N-1}\Lambda^{c_{\alpha}}\frac{\partial\boldsymbol{h}_{\alpha}}{\partial\boldsymbol{A}}+\Lambda^{\boldsymbol{v}}\cdot\frac{\partial\boldsymbol{T}^{*}}{\partial\boldsymbol{A}}+\Lambda^{\boldsymbol{\omega}}\cdot\frac{\partial\boldsymbol{W}^{*}}{\partial\boldsymbol{A}}-\Lambda^{\varepsilon}\frac{\partial\boldsymbol{\phi}^{*}}{\partial\boldsymbol{A}}\right]+$$

$$\mathrm{grad}(c_{\beta})^{+}\cdot\left[\frac{\partial\mathfrak{E}}{\partial\,\mathrm{grad}(c_{\beta})}-\sum_{\alpha=1}^{N-1}\Lambda^{c_{\alpha}}\frac{\partial\boldsymbol{j}_{\alpha}}{\partial\mathrm{grad}(c_{\beta})}+\Lambda^{\boldsymbol{v}}\cdot\frac{\partial\boldsymbol{T}}{\partial\,\mathrm{grad}(c_{\beta})}+\Lambda^{\boldsymbol{\omega}}\cdot\frac{\partial\boldsymbol{W}}{\partial\,\mathrm{grad}(c_{\beta})}-\Lambda^{\varepsilon}\frac{\partial\boldsymbol{\phi}}{\partial\,\mathrm{grad}(c_{\beta})}\right]$$

$$+\nabla[\nabla(c_{\beta})]\cdot\left[\frac{\partial\mathfrak{E}^{*}}{\partial\nabla(c_{\beta})}-\sum_{\alpha=1}^{N-1}\Lambda^{c_{\alpha}}\frac{\partial\boldsymbol{h}_{\alpha}}{\partial\nabla(c_{\beta})}+\Lambda^{\boldsymbol{v}}\cdot\frac{\partial\boldsymbol{T}^{*}}{\partial\nabla(c_{\beta})}+\Lambda^{\boldsymbol{\omega}}\cdot\frac{\partial\boldsymbol{W}^{*}}{\partial\nabla(c_{\beta})}-\Lambda^{\varepsilon}\frac{\partial\boldsymbol{\phi}^{*}}{\partial\nabla(c_{\beta})}\right]+$$

$$\mathrm{grad}(\theta)^{+}\cdot\left[\frac{\partial\mathfrak{E}}{\partial\,\mathrm{grad}(\theta)}-\sum_{\alpha=1}^{N-1}\Lambda^{c_{\alpha}}\frac{\partial\boldsymbol{j}_{\alpha}}{\partial\,\mathrm{grad}(\theta)}+\Lambda^{\boldsymbol{v}}\cdot\frac{\partial\boldsymbol{T}}{\partial\,\mathrm{grad}(\theta)}+\Lambda^{\boldsymbol{\omega}}\cdot\frac{\partial\boldsymbol{W}}{\partial\,\mathrm{grad}(\theta)}-\Lambda^{\varepsilon}\frac{\partial\boldsymbol{\phi}}{\partial\,\mathrm{grad}(\theta)}\right]+$$

$$\nabla[\nabla(\theta)]\cdot\left[\frac{\partial\mathfrak{E}^{*}}{\partial\nabla(\theta)}-\sum_{\alpha=1}^{N-1}\Lambda^{c_{\alpha}}\frac{\partial\boldsymbol{h}_{\alpha}}{\partial\nabla(\theta)}+\Lambda^{\boldsymbol{v}}\cdot\frac{\partial\boldsymbol{T}^{*}}{\partial\nabla(\theta)}+\Lambda^{\boldsymbol{\omega}}\cdot\frac{\partial\boldsymbol{W}^{*}}{\partial\nabla(\theta)}-\Lambda^{\varepsilon}\frac{\partial\boldsymbol{\phi}^{*}}{\partial\nabla(\theta)}\right]+$$

$$\operatorname{grad}(\boldsymbol{\omega})^{+}\cdot\left[\frac{\partial\mathfrak{E}}{\partial\operatorname{grad}(\boldsymbol{\omega})}-\sum_{\alpha=1}^{N-1}\Lambda^{c_\alpha}\frac{\partial\boldsymbol{j}_\alpha}{\partial\operatorname{grad}(\boldsymbol{\omega})}+\Lambda^{\boldsymbol{v}}\cdot\frac{\partial\boldsymbol{T}}{\partial\operatorname{grad}(\boldsymbol{\omega})}+\Lambda^{\boldsymbol{\omega}}\cdot\frac{\partial\boldsymbol{W}}{\partial\operatorname{grad}(\boldsymbol{\omega})}-\Lambda^{\varepsilon}\frac{\partial\boldsymbol{\phi}}{\partial\operatorname{grad}(\boldsymbol{\omega})}\right]$$
$$+\nabla[\nabla(\boldsymbol{\omega})]\cdot\left[\frac{\partial\mathfrak{E}^{*}}{\partial\nabla(\boldsymbol{\omega})}-\sum_{\alpha=1}^{N-1}\Lambda^{c_\alpha}\frac{\partial\boldsymbol{h}_\alpha}{\partial\nabla(\boldsymbol{\omega})}+\Lambda^{\boldsymbol{v}}\cdot\frac{\partial\boldsymbol{T}^{*}}{\partial\nabla(\boldsymbol{\omega})}+\Lambda^{\boldsymbol{\omega}}\cdot\frac{\partial\boldsymbol{W}^{*}}{\partial\nabla(\boldsymbol{\omega})}-\Lambda^{\varepsilon}\frac{\partial\boldsymbol{\phi}^{*}}{\partial\nabla(\boldsymbol{\omega})}\right]$$
$$-\rho\Lambda^{\rho}\boldsymbol{1}\cdot\boldsymbol{D}+\Lambda^{\varepsilon}\boldsymbol{T}:\boldsymbol{D}+\Lambda^{\varepsilon}\boldsymbol{W}^{T}:\operatorname{grad}(\boldsymbol{\omega})-\Lambda^{\varepsilon}(\boldsymbol{T}^{*})^{T}:\nabla(\boldsymbol{v})+\Lambda^{\varepsilon}(\boldsymbol{W}^{*})^{T}:\nabla(\boldsymbol{\omega})$$
$$-\Lambda^{\varepsilon}\boldsymbol{\omega}\cdot\boldsymbol{t}+\sum_{\alpha=1}^{N-1}\Lambda^{c_\alpha}\chi_\alpha\geq 0 \tag{4.38}$$

Analogously to inequality (4.5) and equation (4.6), the inequality (4.38) can be expressed as

$$\mathfrak{T}(\mathscr{Y})\cdot\mathfrak{d}+\mathfrak{P}(\mathscr{Y})\geq 0, \tag{4.39}$$

where, $\mathfrak{T}(\mathscr{Y})$ and $\mathfrak{P}(\mathscr{Y})$ are functions of state variables $\mathscr{Y}$ listed in (4.35), and $\mathfrak{d}$ represents higher derivatives according to

$$\mathfrak{d}\in\left\{\frac{d\rho}{dt},\frac{d}{dt}\operatorname{grad}(\rho),\frac{dc_\alpha}{dt},\frac{d}{dt}\operatorname{grad}(c_\beta),\frac{d\theta}{dt},\frac{d}{dt}\operatorname{grad}(\theta),\frac{d\boldsymbol{w}}{dt},\frac{d\boldsymbol{A}}{dt},\frac{d\boldsymbol{D}}{dt},\frac{d\boldsymbol{v}}{dt},\frac{d\boldsymbol{\omega}}{dt},\frac{d}{dt}\operatorname{grad}(\boldsymbol{\omega}),\right.$$
$$\operatorname{grad}(\rho),\operatorname{grad}(\theta)^{+},\operatorname{grad}(c_\beta)^{+},\operatorname{grad}(\boldsymbol{\omega})^{+},\operatorname{grad}(\boldsymbol{w}),\operatorname{grad}(\boldsymbol{D}),\operatorname{grad}(\boldsymbol{A}),$$
$$\left.\nabla(\rho),\nabla[\nabla(c_\beta)],\nabla(\boldsymbol{w}),\nabla(\boldsymbol{D}),\nabla[\nabla(\boldsymbol{\omega})],\nabla(\boldsymbol{A}),\nabla[\nabla(\theta)]\right\}. \tag{4.40}$$

The inequality (4.39) is linear in $\mathfrak{d}$, and the values of $\mathfrak{d}$ can be given independently of the values of $\mathfrak{T}$ and $\mathfrak{P}$. This implies that $\mathfrak{T}$ must vanish, otherwise, it would be possible to choose some values of $\mathfrak{d}$ such that the inequality was violated. Thus, such arguments lead from (4.39) to the following Liu identities in $\mathcal{M}^6$,

$$
\begin{gathered}
\rho\frac{\partial s}{\partial \rho} - \Lambda^{\rho} - \Lambda^{\varepsilon}\rho\frac{\partial \varepsilon}{\partial \rho} = 0, \\
\rho\frac{\partial s}{\partial c_{\alpha}} - \rho\Lambda^{c_{\alpha}} - \Lambda^{\varepsilon}\rho\frac{\partial \varepsilon}{\partial c_{\alpha}} = 0, \\
\rho\frac{\partial s}{\partial \theta} - \Lambda^{\varepsilon}\rho\frac{\partial \varepsilon}{\partial \theta} = 0, \\
\rho\frac{\partial s}{\partial \operatorname{grad}(c_{\beta})} - \Lambda^{\varepsilon}\rho\frac{\partial \varepsilon}{\partial \operatorname{grad}(c_{\beta})} = 0, \\
\rho\frac{\partial s}{\partial \boldsymbol{D}} - \Lambda^{\varepsilon}\rho\frac{\partial \varepsilon}{\partial \boldsymbol{D}} = 0, \\
\rho\frac{\partial s}{\partial \boldsymbol{A}} - \Lambda^{\varepsilon}\rho\frac{\partial \varepsilon}{\partial \boldsymbol{A}} = 0, \\
\rho\frac{\partial s}{\partial \boldsymbol{w}} - \Lambda^{\varepsilon}\rho\frac{\partial \varepsilon}{\partial \boldsymbol{w}} = 0, \\
\rho\frac{\partial s}{\partial \operatorname{grad}(\boldsymbol{\omega})} - \Lambda^{\varepsilon}\rho\frac{\partial \varepsilon}{\partial \operatorname{grad}(\boldsymbol{\omega})} = 0, \\
\rho\frac{\partial s}{\partial \operatorname{grad}(\theta)} - \Lambda^{\varepsilon}\rho\frac{\partial \varepsilon}{\partial \operatorname{grad}(\theta)} = 0, \\
\rho\frac{\partial s}{\partial \operatorname{grad}(\rho)} - \Lambda^{\varepsilon}\rho\frac{\partial \varepsilon}{\partial \operatorname{grad}(\rho)} = 0, \\
-\rho\Lambda^{\boldsymbol{v}} = 0, \\
-\rho\boldsymbol{I}\Lambda^{\boldsymbol{\omega}} = 0,
\end{gathered}
\tag{4.41}
$$

$$
\begin{gathered}
\frac{\partial \mathfrak{E}}{\partial \rho}-\sum_{\alpha=1}^{N-1} \Lambda^{c_\alpha} \frac{\partial \boldsymbol{j}_\alpha}{\partial \rho}+\Lambda^{\boldsymbol{v}} \cdot \frac{\partial \boldsymbol{T}}{\partial \rho}+\Lambda^{\boldsymbol{\omega}} \cdot \frac{\partial \boldsymbol{W}}{\partial \rho}-\Lambda^{\varepsilon} \frac{\partial \boldsymbol{\phi}}{\partial \rho}=0, \\
\frac{\partial \mathfrak{E}}{\partial \boldsymbol{w}}-\sum_{\alpha=1}^{N-1} \Lambda^{c_\alpha} \frac{\partial \boldsymbol{j}_\alpha}{\partial \boldsymbol{w}}+\Lambda^{\boldsymbol{v}} \cdot \frac{\partial \boldsymbol{T}}{\partial \boldsymbol{w}}+\Lambda^{\boldsymbol{\omega}} \cdot \frac{\partial \boldsymbol{W}}{\partial \boldsymbol{w}}-\Lambda^{\varepsilon} \frac{\partial \boldsymbol{\phi}}{\partial \boldsymbol{w}}=0, \\
\frac{\partial \mathfrak{E}}{\partial \boldsymbol{D}}-\sum_{\alpha=1}^{N-1} \Lambda^{c_\alpha} \frac{\partial \boldsymbol{j}_\alpha}{\partial \boldsymbol{D}}+\Lambda^{\boldsymbol{v}} \cdot \frac{\partial \boldsymbol{T}}{\partial \boldsymbol{D}}+\Lambda^{\boldsymbol{\omega}} \cdot \frac{\partial \boldsymbol{W}}{\partial \boldsymbol{D}}-\Lambda^{\varepsilon} \frac{\partial \boldsymbol{\phi}}{\partial \boldsymbol{D}}=0, \\
\frac{\partial \mathfrak{E}}{\partial \boldsymbol{A}}-\sum_{\alpha=1}^{N-1} \Lambda^{c_\alpha} \frac{\partial \boldsymbol{j}_\alpha}{\partial \boldsymbol{A}}+\Lambda^{\boldsymbol{v}} \cdot \frac{\partial \boldsymbol{T}}{\partial \boldsymbol{A}}+\Lambda^{\boldsymbol{\omega}} \cdot \frac{\partial \boldsymbol{W}}{\partial \boldsymbol{A}}-\Lambda^{\varepsilon} \frac{\partial \boldsymbol{\phi}}{\partial \boldsymbol{A}}=0, \\
\frac{\partial \mathfrak{E}}{\partial \operatorname{grad}(c_\beta)}-\sum_{\alpha=1}^{N-1} \Lambda^{c_\alpha} \left.\frac{\partial \boldsymbol{j}_\alpha}{\partial \operatorname{grad}(c_\beta)}\right|_{\alpha \neq \beta}+\Lambda^{\boldsymbol{v}} \cdot \frac{\partial \boldsymbol{T}}{\partial \operatorname{grad}(c_\beta)}+\Lambda^{\boldsymbol{\omega}} \cdot \frac{\partial \boldsymbol{W}}{\partial \operatorname{grad}(c_\beta)}-\Lambda^{\varepsilon} \frac{\partial \boldsymbol{\phi}}{\partial \operatorname{grad}(c_\beta)}=0, \\
\frac{\partial \mathfrak{E}}{\partial \operatorname{grad}(\theta)}-\sum_{\alpha=1}^{N-1} \Lambda^{c_\alpha} \frac{\partial \boldsymbol{j}_\alpha}{\partial \operatorname{grad}(\theta)}+\Lambda^{\boldsymbol{v}} \cdot \frac{\partial \boldsymbol{T}}{\partial \operatorname{grad}(\theta)}+\Lambda^{\boldsymbol{\omega}} \cdot \frac{\partial \boldsymbol{W}}{\partial \operatorname{grad}(\theta)}-\Lambda^{\varepsilon} \frac{\partial \boldsymbol{\phi}}{\partial \operatorname{grad}(\theta)}=0, \\
\frac{\partial \mathfrak{E}}{\partial \operatorname{grad}(\boldsymbol{\omega})}-\sum_{\alpha=1}^{N-1} \Lambda^{c_\alpha} \frac{\partial \boldsymbol{j}_\alpha}{\partial \operatorname{grad}(\boldsymbol{\omega})}+\Lambda^{\boldsymbol{v}} \cdot \frac{\partial \boldsymbol{T}}{\partial \operatorname{grad}(\boldsymbol{\omega})}+\Lambda^{\boldsymbol{\omega}} \cdot \frac{\partial \boldsymbol{W}}{\partial \operatorname{grad}(\boldsymbol{\omega})}-\Lambda^{\varepsilon} \frac{\partial \boldsymbol{\phi}}{\partial \operatorname{grad}(\boldsymbol{\omega})}=0,
\end{gathered}
\tag{4.42}
$$

$$
\begin{gathered}
\frac{\partial \mathfrak{E}^*}{\partial \rho}-\sum_{\alpha=1}^{N-1} \Lambda^{c_\alpha} \frac{\partial \boldsymbol{h}_\alpha}{\partial \rho}+\Lambda^{\boldsymbol{v}} \cdot \frac{\partial \boldsymbol{T}^*}{\partial \rho}+\Lambda^{\boldsymbol{\omega}} \cdot \frac{\partial \boldsymbol{W}^*}{\partial \rho}-\Lambda^{\varepsilon} \frac{\partial \boldsymbol{\phi}^*}{\partial \rho}=0, \\
\frac{\partial \mathfrak{E}^*}{\partial \boldsymbol{w}}-\sum_{\alpha=1}^{N-1} \Lambda^{c_\alpha} \frac{\partial \boldsymbol{h}_\alpha}{\partial \boldsymbol{w}}+\Lambda^{\boldsymbol{v}} \cdot \frac{\partial \boldsymbol{T}^*}{\partial \boldsymbol{w}}+\Lambda^{\boldsymbol{\omega}} \cdot \frac{\partial \boldsymbol{W}^*}{\partial \boldsymbol{w}}-\Lambda^{\varepsilon} \frac{\partial \boldsymbol{\phi}^*}{\partial \boldsymbol{w}}=0, \\
\frac{\partial \mathfrak{E}^*}{\partial \boldsymbol{D}}-\sum_{\alpha=1}^{N-1} \Lambda^{c_\alpha} \frac{\partial \boldsymbol{h}_\alpha}{\partial \boldsymbol{D}}+\Lambda^{\boldsymbol{v}} \cdot \frac{\partial \boldsymbol{T}^*}{\partial \boldsymbol{D}}+\Lambda^{\boldsymbol{\omega}} \cdot \frac{\partial \boldsymbol{W}^*}{\partial \boldsymbol{D}}-\Lambda^{\varepsilon} \frac{\partial \boldsymbol{\phi}^*}{\partial \boldsymbol{D}}=0, \\
\frac{\partial \mathfrak{E}^*}{\partial \boldsymbol{A}}-\sum_{\alpha=1}^{N-1} \Lambda^{c_\alpha} \frac{\partial \boldsymbol{h}_\alpha}{\partial \boldsymbol{A}}+\Lambda^{\boldsymbol{v}} \cdot \frac{\partial \boldsymbol{T}^*}{\partial \boldsymbol{A}}+\Lambda^{\boldsymbol{\omega}} \cdot \frac{\partial \boldsymbol{W}^*}{\partial \boldsymbol{A}}-\Lambda^{\varepsilon} \frac{\partial \boldsymbol{\phi}^*}{\partial \boldsymbol{A}}=0, \\
\frac{\partial \mathfrak{E}^*}{\partial \nabla(c_\beta)}-\sum_{\alpha=1}^{N-1} \Lambda^{c_\alpha} \left.\frac{\partial \boldsymbol{h}_\alpha}{\partial \nabla(c_\beta)}\right|_{\alpha \neq \beta}+\Lambda^{\boldsymbol{v}} \cdot \frac{\partial \boldsymbol{T}^*}{\partial \nabla(c_\beta)}+\Lambda^{\boldsymbol{\omega}} \cdot \frac{\partial \boldsymbol{W}^*}{\partial \nabla(c_\beta)}-\Lambda^{\varepsilon} \frac{\partial \boldsymbol{\phi}^*}{\partial \nabla(c_\beta)}=0, \\
\frac{\partial \mathfrak{E}^*}{\partial \nabla(\theta)}-\sum_{\alpha=1}^{N-1} \Lambda^{c_\alpha} \frac{\partial \boldsymbol{h}_\alpha}{\partial \nabla(\theta)}+\Lambda^{\boldsymbol{v}} \cdot \frac{\partial \boldsymbol{T}^*}{\partial \nabla(\theta)}+\Lambda^{\boldsymbol{\omega}} \cdot \frac{\partial \boldsymbol{W}^*}{\partial \nabla(\theta)}-\Lambda^{\varepsilon} \frac{\partial \boldsymbol{\phi}^*}{\partial \nabla(\theta)}=0, \\
\frac{\partial \mathfrak{E}^*}{\partial \nabla(\boldsymbol{\omega})}-\sum_{\alpha=1}^{N-1} \Lambda^{c_\alpha} \frac{\partial \boldsymbol{h}_\alpha}{\partial \nabla(\boldsymbol{\omega})}+\Lambda^{\boldsymbol{v}} \cdot \frac{\partial \boldsymbol{T}^*}{\partial \nabla(\boldsymbol{\omega})}+\Lambda^{\boldsymbol{\omega}} \cdot \frac{\partial \boldsymbol{W}^*}{\partial \nabla(\boldsymbol{\omega})}-\Lambda^{\varepsilon} \frac{\partial \boldsymbol{\phi}^*}{\partial \nabla(\boldsymbol{\omega})}=0,
\end{gathered}
\tag{4.43}
$$

as well as to the residual entropy inequality

$$\begin{aligned}\mathfrak{P} = &\left[\frac{\partial \mathfrak{E}}{\partial\, c_\beta} - \sum_{\alpha=1}^{N-1} \Lambda^{c_\alpha} \frac{\partial \boldsymbol{j}_\alpha}{\partial\, c_\beta} + \Lambda^{\boldsymbol{v}} \cdot \frac{\partial \boldsymbol{T}}{\partial\, c_\beta} + \Lambda^{\boldsymbol{\omega}} \cdot \frac{\partial \boldsymbol{W}}{\partial\, c_\beta} - \Lambda^{\varepsilon} \frac{\partial \boldsymbol{\phi}}{\partial\, c_\beta}\right] \cdot \operatorname{grad}(c_\beta) \\ &+ \left[\frac{\partial \mathfrak{E}}{\partial \theta} - \sum_{\alpha=1}^{N-1} \Lambda^{c_\alpha} \frac{\partial \boldsymbol{j}_\alpha}{\partial \theta} + \Lambda^{\boldsymbol{v}} \cdot \frac{\partial \boldsymbol{T}}{\partial \theta} + \Lambda^{\boldsymbol{\omega}} \cdot \frac{\partial \boldsymbol{W}}{\partial \theta} - \Lambda^{\varepsilon} \frac{\partial \boldsymbol{\phi}}{\partial \theta}\right] \cdot \operatorname{grad}(\theta) + \\ &-\rho \Lambda^{\rho} \boldsymbol{1} : \boldsymbol{D} + \Lambda^{\varepsilon} \boldsymbol{T} : \boldsymbol{D} + \Lambda^{\varepsilon} \boldsymbol{W}^T : \operatorname{grad}(\boldsymbol{\omega}) - \Lambda^{\varepsilon} (\boldsymbol{T}^*)^T : \nabla(\boldsymbol{v}) + \Lambda^{\varepsilon} (\boldsymbol{W}^*)^T : \nabla(\boldsymbol{\omega}) \\ &+ \Lambda^{\varepsilon} \boldsymbol{\omega} \cdot \boldsymbol{t} + \Lambda^{\varepsilon} \sum_{\alpha=1}^{N-1} \Lambda^{c_\alpha} \chi_\alpha \geq 0. \end{aligned} \tag{4.44}$$

From identities $(4.41)_{11,12}$ one deduces that

$$\Lambda^{\boldsymbol{v}} = 0 \qquad \text{and} \qquad \Lambda^{\boldsymbol{\omega}} = 0, \tag{4.45}$$

since neither the density nor the inertia momentum tensor can be null. Thence, equation (4.44) can be simplified, producing

$$\begin{aligned}\mathfrak{P} = &\left[\frac{\partial \mathfrak{E}}{\partial\, c_\beta} - \sum_{\alpha=1}^{N-1} \Lambda^{c_\alpha} \frac{\partial \boldsymbol{j}_\alpha}{\partial\, c_\beta} - \Lambda^{\varepsilon} \frac{\partial \boldsymbol{\phi}}{\partial\, c_\beta}\right] \cdot \operatorname{grad}(c_\beta) + \left[\frac{\partial \mathfrak{E}}{\partial \theta} - \sum_{\alpha=1}^{N-1} \Lambda^{c_\alpha} \frac{\partial \boldsymbol{j}_\alpha}{\partial \theta} - \Lambda^{\varepsilon} \frac{\partial \boldsymbol{\phi}}{\partial \theta}\right] \cdot \operatorname{grad}(\theta) \\ &-\rho \Lambda^{\rho} \boldsymbol{1} : \boldsymbol{D} + \Lambda^{\varepsilon} \boldsymbol{T} : \boldsymbol{D} + \Lambda^{\varepsilon} \boldsymbol{W}^T : \operatorname{grad}(\boldsymbol{\omega}) - \Lambda^{\varepsilon} (\boldsymbol{T}^*)^T : \nabla(\boldsymbol{v}) + \Lambda^{\varepsilon} (\boldsymbol{W}^*)^T : \nabla(\boldsymbol{\omega}) + \\ &\Lambda^{\varepsilon} \boldsymbol{\omega} \cdot \boldsymbol{t} + \Lambda^{\varepsilon} \sum_{\alpha=1}^{N-1} \Lambda^{c_\alpha} \chi_\alpha \geq 0. \end{aligned} \tag{4.46}$$

Note that the above equation is slightly different from (4.11) because it does not present the terms $\rho \Lambda^{\rho} \nabla_{\boldsymbol{n}} \cdot (\boldsymbol{w})$ and $\sum_{\alpha=1}^{N-1} \Lambda^{c_\alpha} \nabla_{\boldsymbol{n}} \cdot (\boldsymbol{h}_\alpha)$. This is due to the choice of the constitutive variables $\boldsymbol{w}$ and $\boldsymbol{h}_\alpha$ for this prototype.

4.2.2 Thermodynamic potential

As for prototype 1, one assumes beforehand that the Lagrange multiplier of energy is a function of the empirical temperature θ only, that is, $\Lambda^{\varepsilon} = \Lambda^{\varepsilon}(\theta)$. Then, by cross-differentiation one obtains from $(4.41)_{3,5}$

$$\frac{\partial^2 s}{\partial \boldsymbol{D} \partial \theta} - \Lambda^{\varepsilon} \frac{\partial^2 \varepsilon}{\partial \boldsymbol{D} \partial \theta} = \frac{\partial^2 s}{\partial \theta \partial \boldsymbol{D}} - \Lambda^{\varepsilon} \frac{\partial^2 \varepsilon}{\partial \theta \partial \boldsymbol{D}} - \left(\frac{\partial \Lambda^{\varepsilon}}{\partial \theta}\right) \left(\frac{\partial \varepsilon}{\partial \boldsymbol{D}}\right), \tag{4.47}$$

from which one concludes that $\partial\varepsilon/\partial\boldsymbol{D}=0$, since $\partial\Lambda^{\varepsilon}/\partial\theta\neq 0$. In view of $(4.41)_5$, one also concludes that $\partial\, s/\partial\boldsymbol{D}=0$. Thus, the internal energy and entropy cannot depend on $\boldsymbol{D}$. Likewise, by using $(4.41)_{3,4,6,7,8,9,10}$ one may show that s and ε can neither depend on $\mathrm{grad}(c_\beta)$, $\boldsymbol{A}$, $\boldsymbol{w}$, $\mathrm{grad}(\boldsymbol{\omega})$, and $\mathrm{grad}(\theta)$. Hence, the identities $(4.41)_{1,2,3,5,4,6,7,8,9,10}$ are reduced to the statements

$$\begin{aligned}
\frac{\partial s}{\partial\theta}&=\Lambda^{\varepsilon}\frac{\partial\varepsilon}{\partial\theta},\\
\frac{\partial s}{\partial\rho}=\frac{1}{\rho}\Lambda^{\rho}+\Lambda^{\varepsilon}\frac{\partial\varepsilon}{\partial\rho}&=\Lambda^{\varepsilon}\left(\frac{\partial\varepsilon}{\partial\rho}-\frac{p}{\rho^2}\right),\qquad p:=-\frac{\Lambda^{\rho}}{\Lambda^{\varepsilon}}\rho,\\
\frac{\partial s}{\partial c_\alpha}=\Lambda^{\varepsilon}\frac{\partial\varepsilon}{\partial c_\alpha}+\Lambda^{c_\alpha}&=\Lambda^{\varepsilon}\left(\frac{\partial\varepsilon}{\partial c_\alpha}-\mu_\alpha\right),\qquad \mu_\alpha:=-\frac{\Lambda^{c_\alpha}}{\Lambda^{\varepsilon}},
\end{aligned}\tag{4.48}$$

in which, $\Lambda^{\varepsilon}=\Lambda^{\varepsilon}(\theta)$, $\Lambda^{\rho}=\Lambda^{\rho}(\rho,c_\alpha,\theta)$, $\Lambda^{c_\alpha}=\Lambda^{c_\alpha}(\rho,c_\alpha,\theta)$, $s=s(\rho,c_\alpha,\theta)$ and $\varepsilon=\varepsilon(\rho,c_\alpha,\theta)$.

Starting from (4.48) one may obtain the total differential of the mesoscopic entropy,

$$\begin{aligned}
ds=\Lambda^{\varepsilon}\left[\frac{\partial\varepsilon}{\partial\theta}d\theta+\left(\frac{\partial\varepsilon}{\partial\rho}+\frac{\Lambda^{\rho}}{\Lambda^{\varepsilon}}\frac{1}{\rho}\right)d\rho+\sum_{\alpha=1}^{N-1}\left(\frac{\partial\varepsilon}{\partial c_\alpha}+\frac{\Lambda^{c_\alpha}}{\Lambda^{\varepsilon}}\right)dc_\alpha\right],\ \text{or}\\
ds=\Lambda^{\varepsilon}\left[d\varepsilon-p\left(\frac{1}{\rho^2}\right)d\rho-\sum_{\alpha=1}^{N-1}\mu_\alpha dc_\alpha\right].
\end{aligned}\tag{4.49}$$

This equation is similar to the so-called Gibbs relation also obtained in (4.14). Then, the considerations made for (4.14) also applies to equation (4.49).

Before continuing on, a few remarks on the physical meaning of the Lagrange multipliers Λ^{c_α}, Λ^{ρ} and Λ^{ε} are addressed:

- According to Müller [46] and Liu [47], Λ^{c_α} can be obtained by taking into account a semipermeable membrane, which separates the reacting mixture and one of its constituents α. Thus, excluding the possibility of tangential velocities at the wall and by assuming that the temperature field is continuous at the membrane, one obtains the following jump expression,

$$\left\|-\frac{\Lambda^{c_\alpha}}{\Lambda^{\varepsilon}}+\frac{1}{2}[(\boldsymbol{v}_\alpha-u_{\mathbf{n}})\mathbf{n}]^2\right\|=0\tag{4.50}$$

The first term on the left-hand side of the expression is named chemical potential, μ_α, according to $(4.48)_3$, whereas the second one is the kinetic energy of the motion of the constituent α in relation to the semipermeable wall.

- The definition of Λ^ρ comes from the evaluation of equilibrium conditions for a viscous heat-conducting fluid [1, 71, 72] besides being related to hydrostatic pressure p.

- In this work Λ^ε was assumed to be a universal function dependent only on θ. While this hypothesis is subject to criticism, by now, it seems quite hard to provide a constitutive model for continuum mixtures without accepting that $\Lambda^\varepsilon(\theta)$. Thus, the reliability of the constitutive model provided here deserves to be investigated as well as whether the definition $\Lambda^\varepsilon = 1/\Theta$ is appropriate for non-equilibrium systems in the macroscopic and mesoscopic spaces.

For this prototype, one also obtains the integrability conditions by performing the respective cross differentiations in (4.48). Hence, the following relations are obtained

$$\frac{\partial \mu_\alpha}{\partial \rho} = \frac{\partial}{\partial c_\alpha}\left(\frac{p}{\rho^2}\right), \qquad \frac{\partial \mu_\alpha}{\partial c_\beta} = \frac{\partial \mu_\beta}{\partial c_\alpha}, \qquad (\forall \alpha, \beta = 1, ..., N-1) \tag{4.51}$$

as well as

$$\frac{d(\ln \Lambda^\varepsilon)}{d\theta} = \frac{1}{\Lambda^\varepsilon}\frac{d\Lambda^\varepsilon}{d\theta} = \frac{\partial \mu_\alpha/\partial\theta}{\partial \varepsilon/\partial c_\alpha - \mu_\alpha} = \frac{\partial p/\partial\theta}{(\partial\varepsilon/\partial\rho)\rho^2 - p}, \quad (\forall \alpha, \beta = 1, ..., N-1). \tag{4.52}$$

Equation $(4.51)_2$ is the well-known Gibbs-Duhem expression that describes the relationship among the constituents chemical potential changes in a thermodynamic system. In turn, equation (4.52) is similar to the one used by Müller [46] to identity the empirical temperature θ with the temperature of ideal gases[3].

[3] Integrating (4.52), one obtains

$$\ln\frac{\Lambda^\varepsilon_f}{\Lambda^\varepsilon_i} = -\ln\frac{\Theta_f}{\Theta_i} = \int_{\theta_i}^{\theta_f}\left[\frac{\partial p/\partial\theta}{(\partial\varepsilon/\partial\rho)\rho^2 - p}\right]d\theta,$$

where $\Theta(\theta) = 1/\Lambda^\varepsilon$, or

$$\frac{\Theta_f}{\Theta_i} = \exp\left\{-\int_{\theta_i}^{\theta_f}\left[\frac{\partial p/\partial\theta}{(\partial\varepsilon/\partial\rho)\rho^2 - p}\right]d\theta,\right\}.$$

The integrability conditions (4.51) and (4.52) can be satisfied identically, if the Helmholtz energy $\mathcal{Q}$ is introduced

$$\mathcal{Q} = \varepsilon - \Theta\, s. \tag{4.53}$$

Hence, by computing its total differential and substituting the result into Gibbs equation (4.49) yields

$$d\mathcal{Q} = \frac{p}{\rho^2} d\rho + \sum_{\alpha=1}^{N-1} \mu_\alpha dc_\alpha - s d\Theta, \tag{4.54}$$

which provides the following relations:

$$\frac{\partial \mathcal{Q}}{\partial \rho} = \frac{p}{\rho^2}, \qquad \frac{\partial \mathcal{Q}}{\partial c_\alpha} = \mu_\alpha, \qquad \frac{\partial \mathcal{Q}}{\partial \Theta} = -s. \tag{4.55}$$

Thus, with the choice of $\mathcal{Q}$ and relations (4.55), the integrability conditions (4.51) and (4.52) are automatically satisfied.

In order to conclude this section, it is worth mentioning that even though equations (4.49) and (4.54) are similar to those of classical thermostatic, they are still more comprehensive than the later because they hold for any point of the material body and they are valid under equilibrium and non-equilibrium conditions. Furthermore, the relations deduced in this text take into account the microscopic structure of the particles of the system under study.

4.2.3 Total entropy flux

By regarding Liu's equations (4.42) and (4.43), one defines a flux vector $\mathfrak{L}$ in $\mathbb{R}^3$ and, analogously, another in $\mathfrak{S}^2$, $\mathfrak{L}^*$, so that

$$\mathfrak{L} = \mathfrak{E} - \Lambda^\varepsilon \boldsymbol{\phi} - \Lambda^\varepsilon \sum_{\alpha=1}^{N-1} \mu_\alpha \boldsymbol{j}_\alpha, \tag{4.56}$$

For an ideal gas with equation of state $p = R_{gas}\Theta_{gas}(\theta)\rho$ and $\varepsilon(\theta)$, the above equation leads to the equality $\Theta(\theta) = \Theta_{gas}(\theta)$. This result can be taken as motivation to identify the empirical temperature θ with the temperature of ideal gases.

$$\mathfrak{L}^* = \mathfrak{E}^* - \Lambda^\varepsilon \boldsymbol{\phi}^* - \Lambda^\varepsilon \sum_{\alpha=1}^{N-1} \mu_\alpha \boldsymbol{h}_\alpha. \tag{4.57}$$

Substituting these definitions into the corresponding equations (4.42) and (4.43), one obtains

$$\begin{gathered}
\frac{\partial \mathfrak{L}}{\partial \rho} = \Lambda^\varepsilon \sum_{\alpha=1}^{N-1} \frac{\partial \mu_\alpha}{\partial \rho} \boldsymbol{j}_\alpha, \quad \frac{\partial \mathfrak{L}}{\partial \boldsymbol{w}} = \Lambda^\varepsilon \sum_{\alpha=1}^{N-1} \frac{\partial \mu_\alpha}{\partial \boldsymbol{w}} \boldsymbol{j}_\alpha, \quad \frac{\partial \mathfrak{L}}{\partial \boldsymbol{D}} = \Lambda^\varepsilon \sum_{\alpha=1}^{N-1} \frac{\partial \mu_\alpha}{\partial \boldsymbol{D}} \boldsymbol{j}_\alpha, \\
\frac{\partial \mathfrak{L}}{\partial \boldsymbol{A}} = \Lambda^\varepsilon \sum_{\alpha=1}^{N-1} \frac{\partial \mu_\alpha}{\partial \boldsymbol{A}} \boldsymbol{j}_\alpha, \quad \frac{\partial \mathfrak{L}}{\partial \mathrm{grad}(c_\beta)} = \Lambda^\varepsilon \sum_{\alpha=1}^{N-1} \frac{\partial \mu_\alpha}{\partial \mathrm{grad}(c_\beta)} \boldsymbol{j}_\alpha, \\
\frac{\partial \mathfrak{L}}{\partial \mathrm{grad}(\theta)} = \Lambda^\varepsilon \sum_{\alpha=1}^{N-1} \frac{\partial \mu_\alpha}{\partial \mathrm{grad}(\theta)} \boldsymbol{j}_\alpha, \quad \frac{\partial \mathfrak{L}}{\partial \mathrm{grad}(\boldsymbol{\omega})} = \Lambda^\varepsilon \sum_{\alpha=1}^{N-1} \frac{\partial \mu_\alpha}{\partial \mathrm{grad}(\boldsymbol{\omega})} \boldsymbol{j}_\alpha,
\end{gathered} \tag{4.58}$$

and

$$\begin{gathered}
\frac{\partial \mathfrak{L}^*}{\partial \rho} = \Lambda^\varepsilon \sum_{\alpha=1}^{N-1} \frac{\partial \mu_\alpha}{\partial \rho} \boldsymbol{h}_\alpha, \quad \frac{\partial \mathfrak{L}^*}{\partial \boldsymbol{w}} = \Lambda^\varepsilon \sum_{\alpha=1}^{N-1} \frac{\partial \mu_\alpha}{\partial \boldsymbol{w}} \boldsymbol{h}_\alpha, \quad \frac{\partial \mathfrak{L}^*}{\partial \boldsymbol{D}} = \Lambda^\varepsilon \sum_{\alpha=1}^{N-1} \frac{\partial \mu_\alpha}{\partial \boldsymbol{D}} \boldsymbol{h}_\alpha, \\
\frac{\partial \mathfrak{L}^*}{\partial \boldsymbol{A}} = \Lambda^\varepsilon \sum_{\alpha=1}^{N-1} \frac{\partial \mu_\alpha}{\partial \boldsymbol{A}} \boldsymbol{h}_\alpha, \quad \frac{\partial \mathfrak{L}^*}{\partial \nabla(c_\beta)} = \Lambda^\varepsilon \sum_{\alpha=1}^{N-1} \frac{\partial \mu_\alpha}{\partial \nabla(c_\beta)} \boldsymbol{h}_\alpha, \\
\frac{\partial \mathfrak{L}^*}{\partial \nabla(\theta)} = \Lambda^\varepsilon \sum_{\alpha=1}^{N-1} \frac{\partial \mu_\alpha}{\partial \nabla(\theta)} \boldsymbol{h}_\alpha, \quad \frac{\partial \mathfrak{L}^*}{\partial \nabla(\boldsymbol{\omega})} = \Lambda^\varepsilon \sum_{\alpha=1}^{N-1} \frac{\partial \mu_\alpha}{\partial \nabla(\boldsymbol{\omega})} \boldsymbol{h}_\alpha.
\end{gathered} \tag{4.59}$$

In the above equations, the definition of $\mu_\alpha = -\Lambda^{c_\alpha}/\Lambda^\varepsilon$ was used together with the definitions of the $\Lambda^{\boldsymbol{v}}$ and $\Lambda^{\boldsymbol{\omega}}$ Lagrange multipliers in (4.45). Note that the reduced dependence of Λ^{c_α} is reflected on μ_α, such that $\mu_\alpha(\rho, c_\alpha, \theta)$. Then, since the above derivatives must vanish, the vectors $\mathfrak{L}$ and $\mathfrak{L}^*$ can be functions only of the variables ρ, c_α, θ, and thence, a reasonable assumption, which is compatible with the second law of thermodynamics, is $\mathfrak{L} = 0$, $\mathfrak{L}^* = 0$. Thus, one defines a mesoscopic entropy flow vector in $\mathbb{R}^3$,

$$\mathfrak{E} = \Lambda^\varepsilon \boldsymbol{\phi} - \Lambda^\varepsilon \sum_{\alpha=1}^{N-1} \mu_\alpha \boldsymbol{j}_\alpha = \left(\boldsymbol{\phi} - \sum_{\alpha=1}^{N-1} \mu_\alpha \boldsymbol{j}_\alpha \right) / \Theta, \tag{4.60}$$

and another in $\mathfrak{S}^2$,

$$\mathfrak{E}^* = \Lambda^\varepsilon \boldsymbol{\phi}^* - \Lambda^\varepsilon \sum_{\alpha=1}^{N-1} \mu_\alpha \boldsymbol{h}_\alpha = \left(\boldsymbol{\phi}^* - \sum_{\alpha=1}^{N-1} \mu_\alpha \boldsymbol{h}_\alpha \right) / \Theta. \tag{4.61}$$

As a consequence of these definitions, the total entropy flux in the mesoscopic space is then given by two contributions. The first one (4.60) is identical to that obtained in macroscopic continuum thermodynamics, as for prototype 1. On the other hand, the entropy flux in $\mathfrak{S}^2$(4.61) is defined in terms of a heat flux vector, ϕ^*, and $\boldsymbol{h}_\alpha$. This last vector represents the rotational diffusive flux of the constituent α, which is due to the different orientations of the particles in the mixture.

Note that the entropy flux in $\mathfrak{S}^2$ stems from the microscopic nature of the constituents exclusively, and it can be deduced in mesoscopic space only. In fact, there is no work in macroscopic continuum thermodynamics, even recent publications, stating that the total entropy flux could have some contribution terms coming from the microscopic nature of the particles. However, there are numerous experiments with complex mixtures[4] demonstrating that rotational diffusive fluxes play a critical role in the dynamical behavior of a mixture [73, 74, 75, 76, 77, 78, 79, 80, 81, 82, 83], even in systems where spherical particles are supposed. Thus, such contribution for the total entropy flux, deduced in this text, is not something so strange or experimentally impractical. On the contrary, it may be a theoretical prediction of mesoscopic model, which could be confirmed by experiments in the future.

4.2.4 Residual inequality

The mesoscopic entropy residual inequality may be obtained by using the definitions $(4.48)_{2,3}$ and (4.60) in equation (4.46), producing

$$\mathfrak{P} = \left(\sum_{\alpha=1}^{N-1}\mu_\alpha \boldsymbol{j}_\alpha - \boldsymbol{\phi}\right)\cdot\frac{\mathrm{grad}(\Theta)}{\Theta} - \sum_{\alpha=1}^{N-1}\boldsymbol{j}_\alpha\cdot\mathrm{grd}(\mu_\alpha) + (\boldsymbol{T}+p\boldsymbol{1})\cdot\boldsymbol{D}$$
$$+(\boldsymbol{T}^*)^T:\nabla(\boldsymbol{v}) + (\boldsymbol{W}^*)^T:\nabla(\boldsymbol{\omega}) + \boldsymbol{W}^T:\mathrm{grad}(\boldsymbol{\omega}) - \sum_{r=1}^{R}\mathfrak{F}_r\Omega_r \geq 0. \tag{4.62}$$

Again, $\mathrm{grd}(\mu_\alpha)$ denotes the reduced gradient of μ_α, in which the density is regarded as constant, i.e.,

$$\mathrm{grd}(\mu_\alpha) = \sum_{\beta=1}^{N}\frac{\partial\mu_\alpha}{\partial\, c_\beta}\mathrm{grad}(c_\beta) + \frac{\partial\mu_\alpha}{\partial\theta}\mathrm{grad}(\theta). \tag{4.63}$$

[4] In this category one includes the model presented in this text, polymers, alloys, nanoparticles, colloids, membranes, surfaces, and biological systems, among many others.

Note that in (4.62)

$$\sum_{\alpha=1}^{N-1} \chi_\alpha \mu_\alpha = \sum_{r=1}^{R} \mathfrak{F}_k \Omega_k, \tag{4.64}$$

was also used. Here, $\mathfrak{F}_k = \sum_{\alpha=1} \nu_{\alpha,k}\mu_\alpha$ ($\nu_{\alpha,k}$ is proportional to the corresponding stoichiometric coefficient in the chemical reaction k) is the chemical affinity of reaction k and Ω_k the rate of conversion of k, supposing R independent chemical reactions. Basically, equation (4.64) reflects the fact that every chemical reaction relates to a dissipative mechanism.

4.2.5 Thermodynamic restrictions

As a consequence of (4.62), the thermodynamic equilibrium state at point $(\boldsymbol{n}, \boldsymbol{x}, t)$ requires a set of conditions. In fact, one has the same conditions to ensure a minimum value of the mesoscopic residual entropy production $\mathfrak{P}$ at any point $(\boldsymbol{n}, \boldsymbol{x}, t)$, which are

$$\begin{gathered}\mathfrak{P} : \xi \to X | \xi \in \{\Omega_k, \boldsymbol{D}, \operatorname{grad}(\Theta), \operatorname{grad}(\boldsymbol{\omega}), \operatorname{grd}(\mu_\alpha), \nabla(\boldsymbol{v}), \nabla(\boldsymbol{\omega})\}, \\ \left.\frac{\partial \mathfrak{P}}{\partial \xi}\right|_E = 0, \qquad \left.\left(\frac{\partial^2 \mathfrak{P}}{\partial \xi^2}\right)\right|_E \geq 0,\end{gathered} \tag{4.65}$$

where the index E stands for local equilibrium state.

Thereafter, from inequality (4.62) and equation $(4.65)_1$, the first-order derivatives of the mesoscopic residual entropy production can be given by

$$\left.\frac{\partial \mathfrak{P}}{\partial \operatorname{grad}(\mu_\alpha)}\right|_E = -\boldsymbol{j}_\alpha = 0, \quad (\forall \alpha = 1, ..., N), \tag{4.66}$$

$$\left.\frac{\partial \mathfrak{P}}{\partial \operatorname{grad}(\Theta)}\right|_E = \frac{1}{\Theta}\left(\sum_{\alpha=1}^{N} \mu_\alpha \boldsymbol{j}_\alpha - \boldsymbol{\phi}\right) = 0, \tag{4.67}$$

or yet

$$\left.\frac{\partial \mathfrak{P}}{\partial \operatorname{grad}(\Theta)}\right|_E = \frac{\boldsymbol{\phi}}{\Theta} = 0,$$

$$\left.\frac{\partial \mathfrak{P}}{\partial \operatorname{grad}(\boldsymbol{\omega})}\right|_E = \boldsymbol{W}^T = 0, \tag{4.68}$$

$$\left.\frac{\partial \mathfrak{P}}{\partial \nabla(\boldsymbol{\omega})}\right|_E = (\boldsymbol{W}^*)^T = 0, \tag{4.69}$$

$$\left.\frac{\partial \mathfrak{P}}{\partial \nabla(\boldsymbol{v})}\right|_E = (\boldsymbol{T}^*)^T = 0, \tag{4.70}$$

$$\left.\frac{\partial \mathfrak{P}}{\partial \boldsymbol{D}}\right|_E = \boldsymbol{T} + p\boldsymbol{1} = 0, \tag{4.71}$$

and consequently

$$\boldsymbol{T}\Big|_E = -p\boldsymbol{1},$$

and

$$\left.\frac{\partial \mathfrak{P}}{\partial \Omega_k}\right|_E = -\mathfrak{F}_k = 0, \quad (\forall k = 1, ..., R). \tag{4.72}$$

It is worth mentioning that the variables $\Omega_k, \nabla(\boldsymbol{\omega}), \nabla(\boldsymbol{v})$ are not independent variables, however they depend on the last, especially, of ρ, c_α and $\boldsymbol{w}$. Such dependency is, therefore, one of the reasons for them to be considered in ξ.

Analyzing the derivatives (4.66), (4.67), (4.68), (4.69), (4.70) one notes that at a mesoscopic thermodynamic equilibrium state, there are no diffusive fluxes of species, flux of heat, nor coupling tensors in $\mathbb{R}^3$ and $\mathfrak{S}^2$. In addition, according to the expression (4.71), the stress tensor $\boldsymbol{T}$ is given by the hydrostatic pressure p and thereby, the

definition of Λ^ρ comes from the evaluation of equilibrium conditions for a viscous heat conducting fluid. Moreover, equation (4.72) leads to the well-known local chemical equilibrium condition, which does not require local kinetic equilibrium.

The evaluation of additional constraints, called dynamic, ones could be done by using equation $(4.65)_2$ and hence, well-know equations including the phenomenological coefficients of diffusion, thermal conductivity and viscosity could be obtained. However, such an investigation is not an objective of this work and, thereby, it will not be presented.

4.3 Concavity of the entropy function

In this work, a mesoscopic entropy principle is assumed in order to establish the equilibrium conditions in mesoscopic space. By using this principle, some well-known thermodynamic relations are obtained. Among these relations, one can highlight the Gibbs relation (4.49),

$$ds = \Lambda^\varepsilon \left[\frac{\partial \varepsilon}{\partial \theta} d\theta + \left(\frac{\partial \varepsilon}{\partial \rho} + \frac{\Lambda^\rho}{\Lambda^\varepsilon} \frac{1}{\rho} \right) d\rho \right] = \frac{1}{\Theta} \left[d\varepsilon - p \left(\frac{1}{\rho^2} \right) d\rho \right], \tag{4.73}$$

where the term related to the chemical potential was overlooked[5]. The integrability condition for this equation is

$$\frac{\partial \varepsilon}{\partial \rho} = \frac{p}{\rho^2} - \frac{\theta}{\rho^2} \frac{\partial p}{\partial \theta}. \tag{4.74}$$

According to thermostatics, the entropy of the system is a concave function of the system internal energy and volume [84]. Thus, at each point in the homogeneous system considered by thermostatics, the specific entropy is a concave function of the system specific internal energy and specific volume, $\nu = 1/\rho$, that is, $s(\varepsilon, \nu)$ is a concave function. However, in reference [47] it is demonstrated that the system need not be homogeneous, because $s(\varepsilon, \nu)$ is concave according to the macroscopic continuum mechanics theory as well. Then, considering equation (4.73), one can discuss the con-

[5]This term can be overlooked when all the amounts of substance are constant.

cavity of $s(\varepsilon,\nu)$ according to the mesoscopic entropy principle assumed in this work. Indeed, in terms of the function $s\,(\varepsilon,\rho)$, the Hessian matrix of $s(\varepsilon,\nu)$ is

$$\left[\begin{array}{cc} \dfrac{\partial^2 s}{\partial\varepsilon^2} & \dfrac{\partial^2 s}{\partial\varepsilon\partial\rho} \\ \\ \dfrac{\partial^2 s}{\partial\rho\partial\varepsilon} & \dfrac{\partial^2 s}{\partial\rho^2}+\dfrac{2}{\rho}\dfrac{\partial s}{\partial\rho} \end{array}\right], \tag{4.75}$$

which must be negative definite, that is,

$$\mathfrak{G}^1=\frac{\partial^2 s}{\partial\varepsilon^2}<0\,,\quad \mathfrak{G}^2=\left|\begin{array}{cc} \dfrac{\partial^2 s}{\partial\varepsilon^2} & \dfrac{\partial^2 s}{\partial\varepsilon\partial\rho} \\ \\ \dfrac{\partial^2 s}{\partial\rho\partial\varepsilon} & \dfrac{\partial^2 s}{\partial\rho^2}+\dfrac{2}{\rho}\dfrac{\partial s}{\partial\rho} \end{array}\right|>0. \tag{4.76}$$

Initially, one looks at $\mathfrak{G}^1$. As $\left.\dfrac{\partial s}{\partial\varepsilon}\right|_\rho=\dfrac{1}{\theta}$, this causes $\left.\dfrac{\partial^2 s}{\partial\varepsilon^2}\right|_\rho=-\dfrac{1}{\theta^2}\left.\dfrac{\partial\varepsilon}{\partial\theta}\right|_\rho^{-1}$, hence,

$$\left.\frac{\partial\varepsilon}{\partial\theta}\right|_\rho>0. \tag{4.77}$$

Note that (4.77) is one of the axioms of the thermodynamic theory [85].

The thermodynamic consequences of $\mathfrak{G}^2$ follow from

$$\left.\frac{\partial^2 s}{\partial\varepsilon^2}\right|_\rho\left(\frac{\partial^2 s}{\partial\rho^2}+\frac{2}{\rho}\frac{\partial s}{\partial\rho}\right)-\left(\frac{\partial^2 s}{\partial\varepsilon\partial\rho}\right)^2>0\,. \tag{4.78}$$

Indeed, one deduce that

$$\left.\frac{\partial^2 s}{\partial\varepsilon^2}\right|_\rho=-\frac{1}{\theta^2}\left.\frac{\partial\varepsilon}{\partial\theta}\right|_\rho^{-1},\qquad \frac{\partial^2 s}{\partial\varepsilon\partial\rho}=\frac{1}{\theta^2}\left.\frac{\partial\varepsilon}{\partial\rho}\right|_\theta\left.\frac{\partial\varepsilon}{\partial\theta}\right|_\rho^{-1}, \tag{4.79}$$

and

$$\left.\frac{\partial^2 s}{\partial\rho^2}\right|_\varepsilon+\frac{2}{\rho}\left.\frac{\partial s}{\partial\rho}\right|_\varepsilon=\frac{p}{\rho^2\theta^2}\left.\frac{\partial\theta}{\partial\rho}\right|_\varepsilon-\frac{1}{\rho^2\theta}\left.\frac{\partial p}{\partial\rho}\right|_\varepsilon, \tag{4.80}$$

which by relation

$$\left.\frac{\partial p}{\partial\rho}\right|_\varepsilon=\left.\frac{\partial p}{\partial\rho}\right|_\theta+\left.\frac{\partial p}{\partial\theta}\right|_\rho\left.\frac{\partial\theta}{\partial\rho}\right|_\varepsilon, \tag{4.81}$$

and the integrability condition (4.74), becomes

$$\left.\frac{\partial^2 s}{\partial \rho^2}\right|_{\varepsilon} + \frac{2}{\rho}\left.\frac{\partial s}{\partial \rho}\right|_{\varepsilon} = -\frac{1}{\rho^2 \theta}\left.\frac{\partial p}{\partial \rho}\right|_{\theta} - \frac{1}{\theta^2}\left.\frac{\partial \varepsilon}{\partial \rho}\right|_{\theta}^2 \left.\frac{\partial \varepsilon}{\partial \theta}\right|_{\rho}^{-1} . \tag{4.82}$$

As$\partial\varepsilon/\partial\theta \neq 0$, then condition (4.78) implies that

$$\left.\frac{\partial p}{\partial \rho}\right|_{\theta} > 0\,, \tag{4.83}$$

which is another important thermodynamic inequality [85].

Moreover, further thermodynamic restrictions can be obtained from expressions (4.77) and (4.83), and by assuming the specific volume $\nu = 1/\rho$ in (4.54). Then, with inequality (4.83) and $\left.\dfrac{\partial \mathcal{Q}}{\partial \nu}\right|_{\theta} = -p$, one obtains

$$\left.\frac{\partial^2 \mathcal{Q}}{\partial \nu^2}\right|_{\Theta} > 0. \tag{4.84}$$

In turn, by using inequality (4.77) and $\left.\dfrac{\partial \mathcal{Q}}{\partial \theta}\right|_{\nu} = -s$, one has

$$\left.\frac{\partial^2 \mathcal{Q}}{\partial \theta^2}\right|_{\nu} < 0. \tag{4.85}$$

Similarly, one can deduce

$$\left.\frac{\partial^2 \mathcal{G}}{\partial p^2}\right|_{\theta} < 0, \quad \text{and} \quad \left.\frac{\partial^2 \mathcal{G}}{\partial \theta^2}\right|_{p} < 0, \tag{4.86}$$

which also are thermodynamic constraints. Such inequalities imply that the Helmholtz energy $\mathcal{Q}$ is a concave function of θ, but a convex function of ν, as well as the Gibbs energy $\mathcal{G}$ is a concave function of both θ and p.

Another thermodynamic constraint of particular importance restricts the values of the specific heat at constant pressure, $C_p = \theta \left.\dfrac{\partial s}{\partial \theta}\right|_{p}$, and the specific heat at constant volume, $C_\nu = \theta \left.\dfrac{\partial s}{\partial \theta}\right|_{\nu}$. From the Gibbs relation (4.73), one deduces

$$C_p = C_\nu - \theta \left.\frac{\partial p}{\partial \nu}\right|_{\theta} \left.\frac{\partial \nu}{\partial \theta}\right|_{p}^2, \tag{4.87}$$

which, with the help of expression (4.83), leads to

$$C_p > C_\nu \,. \tag{4.88}$$

Furthermore, by using the definitions of the coefficients of thermal expansion, $\lambda = \frac{1}{\nu}\left.\frac{\partial \nu}{\partial \theta}\right|_p$, and isothermal compressibility, $\kappa = -\frac{1}{\nu}\left.\frac{\partial \nu}{\partial p}\right|_\theta$, one also writes the relation

$$\lambda^2 < \frac{1}{\theta \nu} C_p \kappa. \tag{4.89}$$

In view of these results, then one proposes:

Proposition 4.3 *If the mesoscopic entropy, s, is a concave function of the internal energy, ε, and the volume, ν, then the thermodynamic restrictions* (4.77)*,* (4.83)*,* (4.84)*,* (4.85)*,* (4.86)*,* (4.88) *and* (4.89) *are also valid in $\mathcal{M}^6$.*

Chapter 5

Final remarks

5.1 Conclusions about the work

A mesoscopic continuum thermodynamical description for chemical systems is presented. The proposed model emphasizes mainly the microscopic structure of the solution by recognizing that internal degrees of freedom of constituent particles have an important influence on the physical and chemical properties of the mixture. This is done by introducing the mesoscopic space, $\mathcal{M}^6 = \mathfrak{S}^2 \times \mathbb{R}^3 \times \mathbb{R}^1$, where $\mathfrak{S}^2$ is the space of possible orientations of the microscopic director $\boldsymbol{n}$.

New balance equations are deduced in mesoscopic space. In these equations, more constitutive quantities appear than would be found if the usual macroscopic continuum theory was applied, because additional fluxes in orientation space $\mathfrak{S}^2$ are considered. Basically, such fluxes are constitutive quantities stemming from the intrinsic characteristics of the system particles. The choice of the relevant variables is not obvious, because a great number of them are included in the equations. In fact, the development of prototypes is necessary, in order to test the mesoscopic model considered.

In this work, two prototypes are proposed: the first one considers constitutive quantities defined in $\mathbb{R}^3$ only, while the second one includes constitutive quantities defined in both $\mathbb{R}^3$ and $\mathfrak{S}^2$. Prototype 1 shows some physically incoherent results, but in prototype 2, the findings are in agreement with recent studies in continuum thermodynamics. Furthermore, prototype 2 indicates that the total entropy flux may have some contribution terms coming from the microscopic nature of the particles, specifically from the

rotational diffusive fluxes.

The present work also shows that the mesoscopic and macroscopic constitutive theories are not independent of each other. Indeed, the macroscopic constitutive quantities can be obtained by integrating the mesoscopic ones over all orientations. So, in general, a constitutive equation on the mesoscopic level and the averaging procedure results in a macroscopic constitutive equation containing additional information which is not available from purely macroscopic considerations. In addition, the assumptions concerning the state space cause the internal energy and entropy densities, on the mesoscopic level, to be functions only of the temperature, density and concentrations variables.

Finally it is noteworthy that, at least for the system investigated in this work, the propositions used to define the mesoscopic entropy balance have proven to be a good starting point. Furthermore, one expects this approach may be used to describe other non-equilibrium phenomena in more complex chemical systems such as polymers, carbon fiber, steel, etc.

5.2 Prospect of future studies

Altogether, constitutive theory on the mesoscopic level is more sophisticated than on the macroscopic level due to the increased number of constitutive quantities and to the increased freedom in the choice of the state space. Mesoscopic constitutive quantities may seem very theoretical ones, but they are important for theories of complex materials like fiber reinforced composites, ferrofluids and many others. For these materials the evolution of the orientational order is interesting and relevant. For a fiber reinforced composite, for example, if the fibers are aligned more or less parallel, the mechanical properties are different from those for randomly aligned fibers. In order to distinguish between these cases macroscopically, the alignment tensors are introduced as a measure of the orientational order [12, 86, 87]. Hence, to derive equations of motion for the alignment tensors, mesoscopic balance equations and mesoscopic constitutive equations are needed.

For future works, several reasonable extensions of the state space assumed in prototype 2 are worthy of consideration. The inclusion of higher gradients could lead to

interesting results [88, 89, 90] and to a modified equation for the heat flux. Such an inclusion may be relevant for the alignment tensor dynamics derived from the mesoscopic balance equations, together with the mesoscopic constitutive equations. At this level of alignment tensor equations, practical applications of the theory may be discussed.

Perhaps, an immediate application of the concept presented in this text would be for a mixture of armchair carbon nanotubes, because most of their properties change significantly with the alteration of their unit vector values, generally a pair of unit vectors. As a matter of fact, such unit vectors could be defined and used in the same way as the microscopic director $\boldsymbol{n}$ of this work. In addition, one could also assign a distribution function to such vector pairs, in order to analyze the physical properties of these nanotubes.

Appendix A

Topological notions

A.1 Open and closed sets

Let $\mathcal{A}$ be a topological space and $A \subseteq \mathcal{A}$ any subset of $\mathcal{A}$. The closure of A in $\mathcal{A}$, denoted by $\bar{A}$ is the set,

$$\bar{A} = \bigcap \{R \subseteq \mathcal{A} : R \supseteq A \text{ and } R \text{ is closed in } \mathcal{A}\}. \tag{A.1}$$

The interior of A, denoted by Int$A$, is

$$\text{Int}A = \bigcup \{S \subseteq \mathcal{A} : S \subseteq A \text{ and } S \text{ is open in } \mathcal{A}\}. \tag{A.2}$$

One also defines the exterior of A, denoted by Ext$A$, as

$$\text{Ext}A = \mathcal{A} \setminus \bar{A}, \tag{A.3}$$

and the boundary of A, denoted by ∂A, as

$$\partial A = \mathcal{A} \setminus (\text{Int}A \cup \text{Ext}A). \tag{A.4}$$

It follows from the definitions that for any subset $A \subseteq \mathcal{A}$, the whole space $\mathcal{A}$ is given

by the disjoint union of Int$A$, Ext$A$ and ∂A. Hence, the set A always contains all of its interior points and none of its exterior points, and may contain all, some, or none of its boundary points [91, 92, 93]. These concepts can be visualized by means of the following figure,

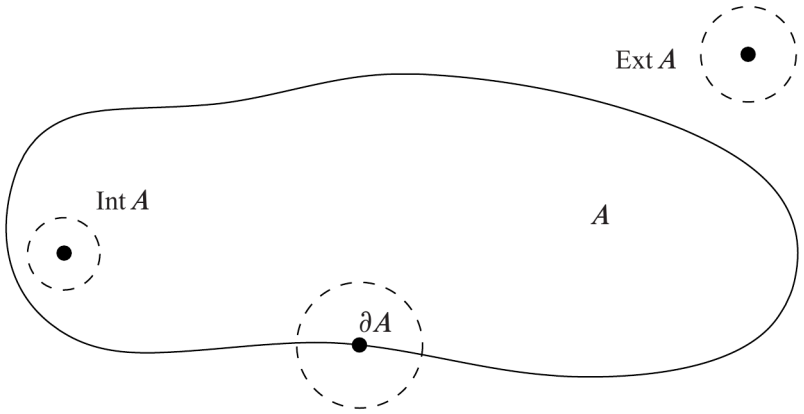

Figure A.1: *Scheme showing the points inside, outside and on the boundary of A. Figure copied from [55].*

Thus, if A is a closed subset in $\mathcal{A}$, one concludes that

- $A = \bar{A}$.
- A contains all of its boundary.
- Every point of $\mathcal{A} \setminus A$ has a neighborhood contained in $\mathcal{A} \setminus A$.

Conversely, if A is a open subset in $\mathcal{A}$, one has

- $A =$ Int$A$.
- A contains none of its boundary points.
- Every point of A has a neighborhood contained in A.

One can deduce from the properties of open and closed subsets that $\bar{A}$ is closed and Int$A$ is the largest open subset contained in A.

In the metric space, the concept of open ball of point inside open ball may be used to explain the significance of Int$A$. For this purpose, $\forall x, y, z \in \mathcal{A}$, let be $\delta = \epsilon - d(x, y)$. Since, $y \in B_\epsilon(x)$ and $z \in B_\delta(y)$, then one has $d(y, z) < \delta$ and

$$d(x,z) \leq d(x,y) + d(y,z) < d(x,y) + \delta = \epsilon. \tag{A.5}$$

Hence, $z \in B_\epsilon(x)$ and thereby, $B_\delta(y) \subseteq B_\epsilon(x)$. To illustrate this statement, the following figure is proposed for $\mathcal{A} = (\mathbb{R}^2, d_2)$,

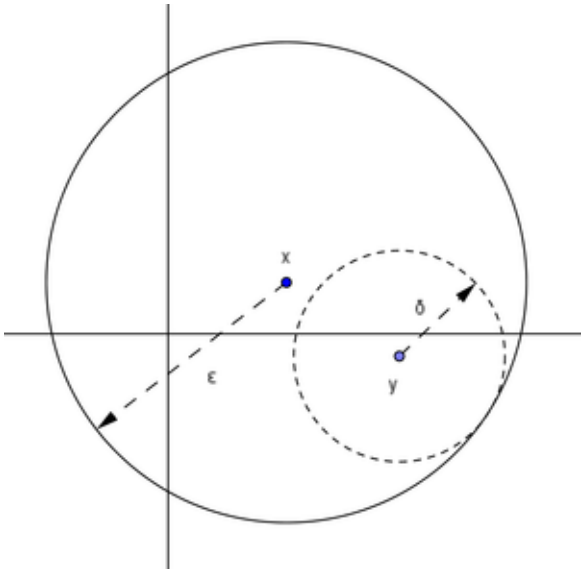

Figure A.2: *Diagram in $\mathbb{R}^2$. A disc radius δ whose center is y and which lies entirely within the larger disc whose center is x with radius ϵ. Figure copied from [91].*

A.2 Product Topologies

The Cartesian product of arbitrary topological spaces is given by $\mathcal{A} = \mathcal{A}_1 \times \mathcal{A}_2 \times ... \times \mathcal{A}_n$. Its product topology is the topology generated by the following base:

$$\mathfrak{X} = \{A_1 \times ... \times A_n; A_i \text{ is a open set of } \mathcal{A}_i, i = 1, ..., n\}. \tag{A.6}$$

The space $\mathcal{A}$ endowed with the product topology is called a product space. The base subsets of the form $A_1 \times ... \times A_n$ are called product open subsets. For example, in the plane $\mathbb{R}^2 = \mathbb{R} \times \mathbb{R}$, the product topology is generated by product open subsets of $\mathbb{R}$. A base for the product topology on $\mathbb{R} \times \mathbb{R}$ consists of open rectangles, which are also a base for the usual topology on $\mathbb{R}^2$. Hence, the product topology in $\mathbb{R} \times \mathbb{R}$ coincides with the usual standard topology in $\mathbb{R}^2$ [91].

Therefore, an analogous justification can be assumed in the mesoscopic space, since it is formed by the Cartesian product of Euclidean manifolds.

A.3 Unit sphere

Let $\mathfrak{S}^n$ be an unit sphere of dimension n. A n-sphere of radius ϵ is defined as the set of points in $\mathbb{R}^{n+1}$, which are at a fixed distance ϵ from a central point. Thus, one defines $\mathfrak{S}^n$ by

$$\mathfrak{S}^n = \left\{ x \in \mathbb{R}^{n+1} : |x| = \epsilon \right\}. \tag{A.7}$$

In particular, when one assumes a sphere of radius $\epsilon = 1$, it is called an unit sphere. Hence, $\mathfrak{S}^n$ is defined as a set of unit-length vectors in $\mathbb{R}^{n+1}$.

The unit sphere $\mathfrak{S}^n$ is not an open set and, thereby, it can not be used as a base set to form the product topology $\tau_{\mathcal{M}}$ of mesoscopic space. A way to bypass this problem is to use the concept of homeomorphism φ through a stereographic projection. The stereographic projection maps all points of $\mathfrak{S}^n$ on an Euclidean space $\mathbb{R}^n$, except one. Let $\mathcal{N} = (0, 0, ..., 1)$ be the excluded point (usually this point is called the north pole), then the stereographic projection $\mathscr{Z} \in \varphi$ can be defined as,

$$\mathscr{Z} : \mathfrak{S}^n \setminus \mathcal{N} \longrightarrow \mathbb{R}^n, (x_1, ..., x_{n+1}) \longmapsto \left(\frac{x_1}{1 - x_{n+1}}, ..., \frac{x_n}{1 - x_{n+1}} \right) = (\xi_1, ..., \xi_n), \tag{A.8}$$

where $(\xi_1, ..., \xi_n)$ are point coordinates into $\mathbb{R}^n$. One can also draw the inverse map $\mathscr{P}^{-1}$, which maps the points of $\mathbb{R}^n$ to $\mathfrak{S}^n$,

$$\mathscr{P}^{-1}(\xi_1, ..., \xi_n) = \left(\frac{2\xi_1}{\xi_1^2 + ... + \xi_n^2 + 1}, ..., \frac{2\xi_n}{\xi_1^2 + ... + \xi_n^2 + 1}, \frac{\xi_1^2 + ... + \xi_n^2 - 1}{\xi_1^2 + ... + \xi_n^2 + 1} \right)$$

Thus, the equivalence between the coordinates is given by

$$\begin{aligned} \xi_1 &= \frac{x_1}{1 - x_{n+1}}, \\ &\vdots \\ \xi_n &= \frac{x_n}{1 - x_{n+1}}, \end{aligned} \tag{A.9}$$

and,

$$
\begin{aligned}
x_1 &= \frac{2\xi_1}{\xi_1^2 + ... + \xi_n^2 + 1}, \\
&\vdots \\
x_n &= \frac{2\xi_n}{\xi_1^2 + ... + \xi_n^2 + 1}, \\
x_{n+1} &= \frac{\xi_1^2 + ... + \xi_n^2 - 1}{\xi_1^2 + ... + \xi_n^2 + 1}.
\end{aligned}
\tag{A.10}
$$

The points set $\{(\xi_1, ..., \xi_n)\}$ is open.

Appendix B

Balance equations

Here, the mathematical steps to obtain the mesoscopic balance equations in terms of the material time derivative are presented.

B.1 Mathematical properties of operators

The properties of gradient and divergent operators are given by following theorem:

Theorem B.1 *Let $f, \boldsymbol{v}, \boldsymbol{w}$ and $\boldsymbol{S}$ be smooth fields, where f is a scalar, $\boldsymbol{v}$ and $\boldsymbol{w}$ vectors, and $\boldsymbol{S}$ a second order tensor. For these fields, one has the following properties:*

$$\operatorname{grad}(f\boldsymbol{v}) = f\ \operatorname{grad}(\boldsymbol{v}) + \boldsymbol{v} \otimes \operatorname{grad}(f), \tag{B.1a}$$

$$\operatorname{div}(f\boldsymbol{v}) = f\ \operatorname{div}(\boldsymbol{v}) + \boldsymbol{v} \cdot \operatorname{grad}(f), \tag{B.1b}$$

$$\operatorname{grad}(\boldsymbol{v} \cdot \boldsymbol{w}) = \boldsymbol{v}\left[\operatorname{grad}(\boldsymbol{w})\right]^T + \boldsymbol{w}\left[\operatorname{grad}(\boldsymbol{v})\right]^T, \tag{B.1c}$$

$$\operatorname{div}(\boldsymbol{v} \otimes \boldsymbol{w}) = \boldsymbol{v}\ \operatorname{div}(\boldsymbol{w}) + \boldsymbol{w}\ \operatorname{grad}(\boldsymbol{v}), \tag{B.1d}$$

$$\operatorname{div}\left(\boldsymbol{S}^T\boldsymbol{v}\right) = \boldsymbol{S} \cdot \operatorname{grad}(\boldsymbol{v}) + \boldsymbol{v} \cdot \operatorname{div}(\boldsymbol{S}), \tag{B.1e}$$

$$\operatorname{div}(f\boldsymbol{S}) = f\ \operatorname{div}(\boldsymbol{S}) + \boldsymbol{S}\ \operatorname{grad}(f) \tag{B.1f}$$

The proof of this theorem is not presented here, but it can be found in reference [94].

B.2 Deduction of the balance equations

In order to derive the local balance equations, one starts from the general balance law for the constituents of the mixture,

$$\frac{\partial}{\partial t}\psi(\cdot) + \operatorname{div}[\psi(\cdot)\boldsymbol{v}(\cdot) + \boldsymbol{\Gamma}_{\psi(\cdot)}] + \nabla_{\boldsymbol{n}} \cdot [\psi(\cdot)\boldsymbol{w}(\cdot) + \boldsymbol{\Gamma}^{*}_{\psi(\cdot)}] = \mathfrak{s}_{\psi(\cdot)} + \mathfrak{p}_{\psi(\cdot)}, \tag{B.2}$$

which holds at all points of the body except on the singular surfaces. In this expression, $(\cdot)$ represents $(\boldsymbol{n}, \boldsymbol{x}, t)$, $\psi(\cdot)$ is a mesoscopic field to be balanced, $\boldsymbol{v}(\cdot)$ is the mesoscopic material velocity, $\boldsymbol{w}(\cdot)$ the mesoscopic change velocity of the microscopic director $\boldsymbol{n}$ in $\mathfrak{S}^2$, $\boldsymbol{\Gamma}_{\psi(\cdot)}$ the non-convective flow of $\psi(\cdot)$ on space $\mathbb{R}^3$, $\boldsymbol{\Gamma}^{*}_{\psi(\cdot)}$ the analogous flow on unit sphere manifold $\mathfrak{S}^2$, $\mathfrak{s}_{\psi(\cdot)}$ the supply, and $\mathfrak{p}_{\psi(\cdot)}$ is the production.

Mass

For mass balance, the variables in (B.2) are defined as follows:

$$\psi_\alpha = \rho_\alpha, \quad \boldsymbol{\Gamma}_\alpha = 0, \quad \boldsymbol{\Gamma}^{*}_{\alpha} = 0, \quad \mathfrak{s}_\alpha = 0, \quad \mathfrak{p}_\alpha = \chi_\alpha.$$

Hence, the mass balance of the constituent α is given by

$$\frac{\partial \rho_\alpha}{dt} + \operatorname{div}(\rho_\alpha \boldsymbol{v}_\alpha) + \nabla_{\boldsymbol{n}} \cdot (\rho_\alpha \boldsymbol{w}_\alpha) = \chi_\alpha. \tag{B.3}$$

By using the propriety (B.1b) in (B.3), one has

$$\frac{\partial \rho_\alpha}{dt} + \boldsymbol{v}_\alpha \cdot \operatorname{grad}(\rho_\alpha) + \rho_\alpha \operatorname{div}(\boldsymbol{v}_\alpha) + \boldsymbol{w}_\alpha \cdot \nabla(\rho_\alpha) + \rho_\alpha \nabla_{\boldsymbol{n}} \cdot (\boldsymbol{w}_\alpha) = \chi_\alpha. \tag{B.4}$$

To simplify this expression, one employs the concept of material derivative,

$$\frac{d^\alpha \rho_\alpha}{dt} = \frac{\partial \rho_\alpha}{dt} + \boldsymbol{v}_\alpha \cdot \operatorname{grad}(\rho_\alpha) + \boldsymbol{w}_\alpha \cdot \nabla(\rho_\alpha), \tag{B.5}$$

then, using (B.5) in (B.4), the mass balance equation for constituent α can be express as

$$\frac{d^{\alpha}\rho_{\alpha}}{dt} + \rho_{\alpha}\,\mathrm{div}(\boldsymbol{v}_{\alpha}) + \rho_{\alpha}\,\nabla_{\boldsymbol{n}}\cdot(\boldsymbol{w}_{\alpha}) = \chi_{\alpha}. \tag{B.6}$$

For the mixture one has

$$\frac{d\rho}{dt} + \rho\,\mathrm{div}(\boldsymbol{v}) + \rho\,\nabla_{\boldsymbol{n}}\cdot(\boldsymbol{w}) = 0, \tag{B.7}$$

where $\sum_{\alpha}\chi_{\alpha} = 0$, $\rho = \sum_{\alpha}\rho_{\alpha}$, $\rho\boldsymbol{v} = \sum_{\alpha}\rho_{\alpha}\boldsymbol{v}_{\alpha}$ and $\rho\boldsymbol{w} = \sum_{\alpha}\rho_{\alpha}\boldsymbol{w}_{\alpha}$.

Concentration

The mass concentration is defined by $c_{\alpha} = \rho_{\alpha}/\rho$ and, for obtaining its balance equation one replaces ρ_{α} by ρc_{α} in (B.3),

$$\frac{\partial\rho c_{\alpha}}{dt} + \mathrm{div}\,(\rho c_{\alpha}\boldsymbol{v}_{\alpha}) + \nabla_{\boldsymbol{n}}\cdot(\rho c_{\alpha}\boldsymbol{w}_{\alpha}) = \chi_{\alpha}. \tag{B.8}$$

To simplify this equation one defines two velocities: translational diffusion velocity $\boldsymbol{u}_{\alpha} = \boldsymbol{v}_{\alpha} - \boldsymbol{v}$ and rotational diffusion velocity $\boldsymbol{\varpi}_{\alpha} = \boldsymbol{w}_{\alpha} - \boldsymbol{w}$. So, replacing these two definitions in (B.8), one has

$$c_{\alpha}\frac{\partial\rho}{dt} + \rho\frac{\partial c_{\alpha}}{dt} + \mathrm{div}(\underbrace{\rho c_{\alpha}\boldsymbol{u}_{\alpha}}_{\boldsymbol{j}_{\alpha}}) + \mathrm{div}\,(\rho c_{\alpha}\boldsymbol{v}) + \nabla_{\boldsymbol{n}}\cdot(\underbrace{\rho c_{\alpha}\boldsymbol{\varpi}_{\alpha}}_{\boldsymbol{h}_{\alpha}}) + \nabla_{\boldsymbol{n}}\cdot(\rho c_{\alpha}\boldsymbol{w}) = \chi_{\alpha}, \tag{B.9}$$

where $\rho c_{\alpha}\boldsymbol{u}_{\alpha} = \boldsymbol{j}_{\alpha}$ and $\rho c_{\alpha}\boldsymbol{\varpi}_{\alpha} = \boldsymbol{h}_{\alpha}$ are named as the translational and rotational diffusive fluxes of constituent α, respectively.

Finally, by using the property (B.1b) in (B.9) and rearranging the terms in the form of material derivative,

$$c_\alpha \Bigg[\underbrace{\frac{d\rho}{dt} + \rho \operatorname{div}(\boldsymbol{v}) + \rho \nabla_{\boldsymbol{n}} \cdot (\boldsymbol{w})}_{=0} \Bigg] + \rho \Bigg[\underbrace{\frac{\partial c_\alpha}{dt} + \boldsymbol{v} \cdot \operatorname{grad}(c_\alpha) + \boldsymbol{w} \cdot \nabla(c_\alpha)}_{dc_\alpha/dt} \Bigg]$$

$$+ \operatorname{div}(\boldsymbol{j}_\alpha) + \nabla_{\boldsymbol{n}} \cdot (\boldsymbol{h}_\alpha) = \chi_\alpha,$$

$$\Updownarrow$$

$$\rho \frac{dc_\alpha}{dt} + \operatorname{div}(\boldsymbol{j}_\alpha) + \nabla_{\boldsymbol{n}} \cdot (\boldsymbol{h}_\alpha) = \chi_\alpha, \qquad (\alpha = 1, ..., N), \tag{B.10}$$

which is valid for all constituents. In the case of concentration balance for the mixture

$$\sum_{\alpha=1}^{N-1} \Bigg[\rho \frac{dc_\alpha}{dt} + \operatorname{div}(\boldsymbol{j}_\alpha) + \nabla_{\boldsymbol{n}} \cdot (\boldsymbol{h}_\alpha) - \chi_\alpha \Bigg] = 0. \tag{B.11}$$

Linear momentum

For momentum balance, the variables in (B.2) are defined as follows:

$$\psi_\alpha = \rho_\alpha \boldsymbol{v}, \quad \boldsymbol{\Gamma}_\alpha = -\boldsymbol{T}_\alpha, \quad \Gamma^*_\alpha = -\boldsymbol{T}^*_\alpha, \quad \mathfrak{s}_\alpha = \rho_\alpha \boldsymbol{f}_\alpha, \quad \mathfrak{p}_\alpha = \boldsymbol{o}_\alpha.$$

So, the momentum balance is

$$\frac{\partial \rho_\alpha \boldsymbol{v}_\alpha}{dt} + \operatorname{div}(\rho_\alpha \boldsymbol{v}_\alpha \otimes \boldsymbol{v}_\alpha - \boldsymbol{T}_\alpha) + \nabla_{\boldsymbol{n}} \cdot (\rho_\alpha \boldsymbol{v}_\alpha \otimes \boldsymbol{w}_\alpha - \boldsymbol{T}^*_\alpha) = \rho_\alpha \boldsymbol{f}_\alpha + \boldsymbol{o}_\alpha, \tag{B.12}$$

where $\boldsymbol{T}_\alpha$ is the Cauchy stress tensor, $\boldsymbol{T}^*_\alpha$ its analogue defined in $\mathfrak{S}^2$, $\rho_\alpha \boldsymbol{f}_\alpha$ is the momentum supply density exercised by external force on the system and $\boldsymbol{o}_\alpha$ the linear momentum production of the other constituents of the solution for the constituent α.

By using the property (B.1d) into (B.12), the terms $\operatorname{div}(\rho_\alpha \boldsymbol{v}_\alpha \otimes \boldsymbol{v}_\alpha)$ and $\nabla_{\boldsymbol{n}} \cdot (\rho_\alpha \boldsymbol{v}_\alpha \otimes \boldsymbol{w}_\alpha)$ can be written as

$$\operatorname{div}(\rho_\alpha \boldsymbol{v}_\alpha \otimes \boldsymbol{v}_\alpha) = \overbrace{\rho_\alpha \boldsymbol{v}_\alpha \operatorname{grad}(\boldsymbol{v}_\alpha) + \boldsymbol{v}_\alpha [\boldsymbol{v}_\alpha \otimes \operatorname{grad}(\rho_\alpha)]}^{\boldsymbol{v}_\alpha \operatorname{grad}(\rho_\alpha \boldsymbol{v}_\alpha)} + \rho_\alpha \boldsymbol{v}_\alpha \operatorname{div}(\boldsymbol{v}_\alpha),$$

$$\nabla_{\boldsymbol{n}} \cdot (\rho_\alpha \boldsymbol{v}_\alpha \otimes \boldsymbol{w}_\alpha) = \overbrace{\rho_\alpha \boldsymbol{w}_\alpha \nabla(\boldsymbol{v}_\alpha) + \boldsymbol{w}_\alpha [\boldsymbol{v}_\alpha \otimes \nabla(\rho_\alpha)]}^{\boldsymbol{w}_\alpha \nabla(\rho_\alpha \boldsymbol{v}_\alpha)} + \rho_\alpha \boldsymbol{v}_\alpha \nabla_{\boldsymbol{n}} \cdot (\boldsymbol{w}_\alpha).$$

Note that the property (B.1a) has been used. In order to eliminate the tensor product operator ($\otimes$), the concept of linear transformation from a vector space to another is employed according to the following definition.

Definition B.1 *For any vector $\boldsymbol{a} \in A$ and $\boldsymbol{b} \in B$, the tensor product of $\boldsymbol{a}$ and $\boldsymbol{b}$, denoted by $\boldsymbol{a} \otimes \boldsymbol{b}$, is defined as a linear transformation from B to A, such that*

$$\boldsymbol{a} \otimes \boldsymbol{b}(\boldsymbol{c}) = (\boldsymbol{b} \cdot \boldsymbol{c})\boldsymbol{a},$$

for any $\boldsymbol{c} \in B$.

Hence, the relations for the divergent can be described as

$$\begin{aligned}
\operatorname{div}(\rho_\alpha \boldsymbol{v}_\alpha \otimes \boldsymbol{v}_\alpha) &= \rho_\alpha \boldsymbol{v}_\alpha \operatorname{grad}(\boldsymbol{v}_\alpha) + \boldsymbol{v}_\alpha[\boldsymbol{v}_\alpha \cdot \operatorname{grad}(\rho_\alpha)] + \rho_\alpha \boldsymbol{v}_\alpha \operatorname{div}(\boldsymbol{v}_\alpha), \\
\nabla_{\boldsymbol{n}} \cdot (\rho_\alpha \boldsymbol{v}_\alpha \otimes \boldsymbol{w}_\alpha) &= \rho_\alpha \boldsymbol{w}_\alpha \nabla(\boldsymbol{v}_\alpha) + \boldsymbol{v}_\alpha[\boldsymbol{w}_\alpha \cdot \nabla(\rho_\alpha)] + \rho_\alpha \boldsymbol{v}_\alpha \nabla_{\boldsymbol{n}} \cdot (\boldsymbol{w}_\alpha).
\end{aligned}$$

Inserting these definitions in (B.12) and opening the partial derivatives, one obtains

$$\begin{aligned}
\boldsymbol{v}_\alpha \frac{\partial \rho_\alpha}{dt} + \rho_\alpha \frac{\partial \boldsymbol{v}_\alpha}{dt} - \operatorname{div}(\boldsymbol{T}_\alpha) - \nabla_{\boldsymbol{n}} \cdot (\boldsymbol{T}^*_\alpha) + \rho_\alpha \boldsymbol{v}_\alpha \operatorname{grad}(\boldsymbol{v}_\alpha) + \boldsymbol{v}_\alpha[\boldsymbol{v}_\alpha \cdot \operatorname{grad}(\rho_\alpha)] + \rho_\alpha \boldsymbol{v}_\alpha \operatorname{div}(\boldsymbol{v}_\alpha) \\
+\rho_\alpha \boldsymbol{w}_\alpha \nabla(\boldsymbol{v}_\alpha) + \boldsymbol{v}_\alpha[\boldsymbol{w}_\alpha \cdot \nabla(\rho_\alpha)] + \rho_\alpha \boldsymbol{v}_\alpha \nabla_{\boldsymbol{n}} \cdot (\boldsymbol{w}_\alpha) = \rho_\alpha \boldsymbol{f}_\alpha + \boldsymbol{o}_\alpha, \qquad \text{(B.13)}
\end{aligned}$$

which on rearranging produce

$$\begin{aligned}
&\boldsymbol{v}_\alpha \underbrace{\left[\underbrace{\frac{\partial \rho_\alpha}{dt} + \boldsymbol{v}_\alpha \cdot \operatorname{grad}(\rho_\alpha) + \boldsymbol{w}_\alpha \cdot \nabla(\rho_\alpha)}_{d^\alpha \rho_\alpha / dt} + \rho_\alpha \operatorname{div}(\boldsymbol{v}_\alpha) + \rho_\alpha \nabla_{\boldsymbol{n}} \cdot (\boldsymbol{w}_\alpha) \right]}_{\chi_\alpha} \\
&+\rho_\alpha \underbrace{\left[\frac{\partial \boldsymbol{v}_\alpha}{dt} + \boldsymbol{v}_\alpha \operatorname{grad}(\boldsymbol{v}_\alpha) + \boldsymbol{v}_\alpha \nabla(\boldsymbol{w}_\alpha) \right]}_{d^\alpha \boldsymbol{v}_\alpha / dt} - \operatorname{div}(\boldsymbol{T}_\alpha) - \nabla_{\boldsymbol{n}} \cdot (\boldsymbol{T}^*_\alpha) = \rho_\alpha \boldsymbol{f}_\alpha + \boldsymbol{o}_\alpha,
\end{aligned}$$

and, hence

$$\rho_\alpha \frac{d^\alpha \boldsymbol{v}_\alpha}{dt} - \operatorname{div}(\boldsymbol{T}_\alpha) - \nabla_{\boldsymbol{n}} \cdot (\boldsymbol{T}^*_\alpha) = \rho_\alpha \boldsymbol{f}_\alpha + (\boldsymbol{o}_\alpha - \boldsymbol{v}_\alpha \chi_\alpha), \qquad \text{(B.14)}$$

Thus, for the solution

$$\rho\frac{d\boldsymbol{v}}{dt} - \operatorname{div}(\boldsymbol{T}) - \nabla_{\boldsymbol{n}} \cdot (\boldsymbol{T}^*) = \rho\boldsymbol{f}, \tag{B.15}$$

where,

$$\sum_{\alpha}(\boldsymbol{o}_\alpha - \boldsymbol{v}_\alpha\chi_\alpha) = 0, \quad \rho\boldsymbol{f} = \sum_{\alpha}\rho_\alpha\boldsymbol{f}_\alpha,$$
$$\boldsymbol{T} = \sum_{\alpha}\boldsymbol{T}_\alpha - \sum_{\alpha}\rho_\alpha\boldsymbol{u}_\alpha \otimes \boldsymbol{u}_\alpha,$$
$$\boldsymbol{T}^* = \sum_{\alpha}\boldsymbol{T}^*_\alpha - \sum_{\alpha}\rho_\alpha\boldsymbol{\varpi}_\alpha \otimes \boldsymbol{\varpi}_\alpha.$$

Angular velocity

Starting from

$$\psi_\alpha = \rho_\alpha\boldsymbol{s}_\alpha + \boldsymbol{x} \times \rho_\alpha\boldsymbol{v}_\alpha, \quad \boldsymbol{\Gamma}_\alpha = -\boldsymbol{x} \times \boldsymbol{T}_\alpha - \boldsymbol{W}_\alpha, \quad \Gamma^*_\alpha = -\boldsymbol{x} \times \boldsymbol{T}^*_\alpha - \boldsymbol{W}^*_\alpha,$$
$$\mathfrak{s}_\alpha = \boldsymbol{x} \times \rho_\alpha\boldsymbol{f}_\alpha + \rho_\alpha\boldsymbol{g}_\alpha, \quad \mathfrak{p}_\alpha = \boldsymbol{x} \times \boldsymbol{o}_\alpha + \boldsymbol{i}_\alpha,$$

the angular momentum balance can be expressed as

$$\frac{\partial}{\partial t}(\rho_\alpha\boldsymbol{s}_\alpha + \boldsymbol{x} \times \rho_\alpha\boldsymbol{v}_\alpha) + \operatorname{div}\Big[(\rho_\alpha\boldsymbol{s}_\alpha + \boldsymbol{x} \times \rho_\alpha\boldsymbol{v}_\alpha) \otimes \boldsymbol{v}_\alpha - \boldsymbol{x} \times \boldsymbol{T}_\alpha - \boldsymbol{W}_\alpha\Big]$$
$$+\nabla_{\boldsymbol{n}} \cdot \Big[(\rho_\alpha\boldsymbol{s}_\alpha + \boldsymbol{x} \times \rho_\alpha\boldsymbol{v}_\alpha) \otimes \boldsymbol{w}_\alpha - \boldsymbol{x} \times \boldsymbol{T}^*_\alpha - \boldsymbol{W}^*_\alpha\Big] = \boldsymbol{x} \times \rho_\alpha\boldsymbol{f}_\alpha + \rho_\alpha\boldsymbol{g}_\alpha$$
$$+\boldsymbol{x} \times \boldsymbol{o}_\alpha + \boldsymbol{i}_\alpha. \tag{B.16}$$

Here, $\boldsymbol{x}$ is the position vector, $\boldsymbol{s}$ the spin vector, $\boldsymbol{W}_\alpha$ the mesoscopic surface torque or coupled stress on $\mathbb{R}^3$ and $\boldsymbol{W}^*_\alpha$ its analogous on $\mathfrak{S}^2$, $\rho_\alpha\boldsymbol{g}_\alpha$ is the angular momentum density exerted by external forces on the mesoscopic spin and $\boldsymbol{i}_\alpha$ the specific production of spin.

By analyzing (B.16), one realizes that the terms can be grouped as follows,

$$\frac{\partial \rho_\alpha \boldsymbol{s}_\alpha}{\partial t} + \operatorname{div}(\rho_\alpha \boldsymbol{s}_\alpha \otimes \boldsymbol{v}_\alpha) - \operatorname{div}(\boldsymbol{W}_\alpha) + \nabla_{\boldsymbol{n}} \cdot (\rho_\alpha \boldsymbol{s}_\alpha \otimes \boldsymbol{w}_\alpha) - \nabla_{\boldsymbol{n}} \cdot (\boldsymbol{W}^*_\alpha)$$
$$+ \boldsymbol{x} \times \Bigg[\underbrace{\frac{\partial \rho_\alpha \boldsymbol{v}_\alpha}{\partial t} + \operatorname{div}(\rho_\alpha \boldsymbol{v}_\alpha \otimes \boldsymbol{v}_\alpha - \boldsymbol{T}_\alpha) + \nabla_{\boldsymbol{n}} \cdot (\rho_\alpha \boldsymbol{v}_\alpha \otimes \boldsymbol{w}_\alpha - \boldsymbol{T}^*_\alpha) - \rho_\alpha \boldsymbol{f}_\alpha - \boldsymbol{o}_\alpha}_{=0 \text{ (linear momentum, see definition } B.12)} \Bigg]$$
$$- \boldsymbol{t}_\alpha = \rho_\alpha \boldsymbol{g}_\alpha + \boldsymbol{i}_\alpha,$$

In fact, $\operatorname{div}(\boldsymbol{x} \times \boldsymbol{T})$ is defined in component form as (to simplify the notation, the index α is omitted in the next two equations)

$$\operatorname{div}(\boldsymbol{x} \times \boldsymbol{T}) = (\epsilon_{ijk} x_i T_{[jl]})_{,l} = \epsilon_{ijk} x_i T_{[jl],l} + \epsilon_{ijk} x_{i,l} T_{[jl]}.$$

But, because $x_{i,l} = \delta_{il}$, the equation above reduces to

$$\operatorname{div}(\boldsymbol{x} \times \boldsymbol{T}) = \epsilon_{ijk} x_i T_{[jl],l} + \epsilon_{ijk} T_{[ji]} = \boldsymbol{x} \times \operatorname{div}(\boldsymbol{T}) + \underbrace{\epsilon_{ijk} T_{[ji]}}_{\boldsymbol{t}}.$$

The dual vector $\boldsymbol{t}_\alpha$ corresponds to the antisymmetric part of the stress tensor $\boldsymbol{T}_\alpha$, that is, $\boldsymbol{t}_\alpha = 0$ if T_α is symmetric. Moreover, $\nabla_{\boldsymbol{n}} \cdot (\boldsymbol{x} \times \boldsymbol{T}^*_\alpha) = \boldsymbol{x} \times \nabla_{\boldsymbol{n}} \cdot (\boldsymbol{T}^*_\alpha)$, because $\boldsymbol{x}$ does not depend of $\boldsymbol{n}$. So, one has

$$\frac{\partial \rho_\alpha \boldsymbol{s}_\alpha}{\partial t} + \operatorname{div}(\rho_\alpha \boldsymbol{s}_\alpha \otimes \boldsymbol{v}_\alpha) - \operatorname{div}(\boldsymbol{W}_\alpha) + \nabla_{\boldsymbol{n}} \cdot (\rho_\alpha \boldsymbol{s}_\alpha \otimes \boldsymbol{w}_\alpha) - \nabla_{\boldsymbol{n}} \cdot (\boldsymbol{W}^*_\alpha) - \boldsymbol{t}_\alpha$$
$$= \rho_\alpha \boldsymbol{g}_\alpha + \boldsymbol{i}_\alpha. \tag{B.17}$$

Thus, according to the relations (B.1d), (B.1a) and equation (B.17), one obtains

$$\boldsymbol{s}_\alpha \Bigg[\underbrace{\frac{\partial \rho_\alpha}{\partial t} + \boldsymbol{v}_\alpha \cdot \operatorname{grad}(\rho_\alpha) + \boldsymbol{w}_\alpha \cdot \nabla(\rho_\alpha) + \rho_\alpha \operatorname{div}(\boldsymbol{v}_\alpha) + \rho_\alpha \nabla_{\boldsymbol{n}} \cdot (\boldsymbol{w}_\alpha)}_{\chi_\alpha} \Bigg]$$
$$+ \rho_\alpha \Bigg[\underbrace{\frac{\partial \boldsymbol{s}_\alpha}{\partial t} + \boldsymbol{v}_\alpha \cdot \operatorname{grad}(\boldsymbol{s}_\alpha) + \boldsymbol{w}_\alpha \cdot \nabla(\boldsymbol{s}_\alpha)}_{d^\alpha \boldsymbol{s}_\alpha / dt} \Bigg] - \operatorname{div}(\boldsymbol{W}_\alpha) - \nabla_{\boldsymbol{n}} \cdot (\boldsymbol{W}^*_\alpha) - \boldsymbol{t}_\alpha$$
$$= \rho_\alpha \boldsymbol{g}_\alpha + \boldsymbol{i}_\alpha,$$

which is equivalent to the spin balance equation

$$\rho_\alpha \frac{d^\alpha \boldsymbol{s}_\alpha}{dt} - \operatorname{div}(\boldsymbol{W}_\alpha) - \nabla_{\boldsymbol{n}} \cdot (\boldsymbol{W}^*_\alpha) - \boldsymbol{t}_\alpha = \rho_\alpha \boldsymbol{g}_\alpha + \boldsymbol{i}_\alpha - \boldsymbol{s}_\alpha \chi_\alpha. \tag{B.18}$$

Considering the definition of spin $\boldsymbol{s}_\alpha = \boldsymbol{I}_\alpha \boldsymbol{\omega}_\alpha$ and the mixture as a micro-polar medium $d^\alpha \boldsymbol{I}_\alpha / dt = 0$, one obtains

$$\rho_\alpha \boldsymbol{I}_\alpha \frac{d^\alpha \boldsymbol{\omega}_\alpha}{dt} - \operatorname{div}(\boldsymbol{W}_\alpha) - \nabla_{\boldsymbol{n}} \cdot (\boldsymbol{W}^*_\alpha) - \boldsymbol{t}_\alpha = \rho_\alpha \boldsymbol{g}_\alpha + \boldsymbol{i}_\alpha - \boldsymbol{s}_\alpha \chi_\alpha. \tag{B.19}$$

This equation represents the balance of angular velocity. For the mixture one has

$$\rho \boldsymbol{I} \frac{d\boldsymbol{\omega}}{dt} - \operatorname{div}(\boldsymbol{W}) - \nabla_{\boldsymbol{n}} \cdot (\boldsymbol{W}^*) - \boldsymbol{t} = \rho \boldsymbol{g}, \tag{B.20}$$

where

$$\rho \boldsymbol{I} = \sum_{\alpha=1}^{N} \rho_\alpha \boldsymbol{I}_\alpha, \quad \rho \boldsymbol{I} \boldsymbol{\omega} = \sum_{\alpha=1}^{N} \rho_\alpha \boldsymbol{I}_\alpha \boldsymbol{\omega}_\alpha, \quad \sum_{\alpha=1}^{N} (\boldsymbol{i}_\alpha - \boldsymbol{s}_\alpha \chi_\alpha) = 0,$$

$$\rho \boldsymbol{g} = \sum_{\alpha=1}^{N} \rho_\alpha \boldsymbol{g}_\alpha, \quad \boldsymbol{t} = \sum_{\alpha=1}^{N} \boldsymbol{t}_\alpha,$$

$$\boldsymbol{W} = \sum_{\alpha=1}^{N} \boldsymbol{W}_\alpha - \sum_{\alpha=1}^{N} \rho_\alpha \boldsymbol{s}_\alpha \otimes \boldsymbol{u}_\alpha, \quad \boldsymbol{W}^* = \sum_{\alpha=1}^{N} \boldsymbol{W}^*_\alpha - \sum_{\alpha=1}^{N} \rho_\alpha \boldsymbol{s}_\alpha \otimes \boldsymbol{\varpi}_\alpha.$$

Internal energy

For this balance, the variables in (B.2) are defined as :

$$\psi_\alpha = \rho_\alpha \varepsilon_\alpha + \frac{1}{2} \rho_\alpha \boldsymbol{v}_\alpha \cdot \boldsymbol{v}_\alpha + \frac{1}{2} \rho_\alpha \boldsymbol{s}_\alpha \cdot \boldsymbol{\omega}_\alpha, \quad \boldsymbol{\Gamma}_\alpha = -\boldsymbol{v}_\alpha \boldsymbol{T}_\alpha - \boldsymbol{\omega}_\alpha \boldsymbol{W}_\alpha + \boldsymbol{\phi},$$

$$\boldsymbol{\Gamma}^*_\alpha = -\boldsymbol{v}_\alpha \boldsymbol{T}^*_\alpha - \boldsymbol{w}_\alpha \boldsymbol{W}^*_\alpha + \boldsymbol{\phi}^*, \quad \mathfrak{s}_\alpha = \boldsymbol{v}_\alpha \cdot \rho_\alpha \boldsymbol{f}_\alpha + \boldsymbol{w}_\alpha \cdot \rho_\alpha \boldsymbol{g}_\alpha + \rho_\alpha r_\alpha, \quad \mathfrak{p}_\alpha = \mathfrak{e}_\alpha.$$

Thus, the energy balance of the constituent α is given by

$$\frac{\partial}{\partial t}\left(\rho_\alpha\varepsilon_\alpha+\frac{1}{2}\rho_\alpha\boldsymbol{v}_\alpha\cdot\boldsymbol{v}_\alpha+\frac{1}{2}\rho_\alpha\boldsymbol{s}_\alpha\cdot\boldsymbol{\omega}_\alpha\right)+\operatorname{div}\left[\left(\rho_\alpha\varepsilon_\alpha+\frac{1}{2}\rho_\alpha\boldsymbol{v}_\alpha\cdot\boldsymbol{v}_\alpha+\frac{1}{2}\rho_\alpha\boldsymbol{s}_\alpha\cdot\boldsymbol{\omega}_\alpha\right)\boldsymbol{v}_\alpha\right]$$
$$+\operatorname{div}\left(-\boldsymbol{v}_\alpha\boldsymbol{T}_\alpha-\boldsymbol{\omega}_\alpha\boldsymbol{W}_\alpha+\boldsymbol{\phi}_\alpha\right)+\nabla_{\boldsymbol{n}}\cdot\left[\left(\rho_\alpha\varepsilon_\alpha+\frac{1}{2}\rho_\alpha\boldsymbol{v}_\alpha\cdot\boldsymbol{v}_\alpha+\frac{1}{2}\rho_\alpha\boldsymbol{s}_\alpha\cdot\boldsymbol{\omega}_\alpha\right)\boldsymbol{w}_\alpha\right]$$
$$\nabla_{\boldsymbol{n}}\cdot\left(-\boldsymbol{v}_\alpha\boldsymbol{T}^*_\alpha-\boldsymbol{\omega}_\alpha\boldsymbol{T}^*_\alpha+\boldsymbol{\phi}^*_\alpha\right)=\boldsymbol{v}_\alpha\cdot\rho_\alpha\boldsymbol{f}_\alpha+\boldsymbol{w}_\alpha\cdot\rho_\alpha\boldsymbol{g}_\alpha+\rho_\alpha r_\alpha+\mathfrak{e}_\alpha. \tag{B.21}$$

In this equation ε_α is the specific internal energy, $\boldsymbol{\phi}_\alpha$ and $\boldsymbol{\phi}^*_\alpha$ are heat flux vectors defined in $\mathbb{R}^3$ and $\mathfrak{S}^2$, respectively. The scalar r_α is the supply related to external radiation and $\mathfrak{e}_\alpha$ the internal energy production. Employing the (B.1b) and (B.1c) properties and grouping the terms in (B.21), one has

$$\rho_\alpha\underbrace{\left[\frac{\partial\varepsilon_\alpha}{\partial t}+\boldsymbol{v}_\alpha\cdot\operatorname{grad}(\varepsilon_\alpha)+\boldsymbol{w}_\alpha\cdot\nabla(\varepsilon_\alpha)\right]}_{d^\alpha\varepsilon_\alpha/dt}$$
$$+\frac{1}{2}\boldsymbol{v}_\alpha\cdot\boldsymbol{v}_\alpha\underbrace{\left[\frac{\partial\rho_\alpha}{\partial t}+\boldsymbol{v}_\alpha\cdot\operatorname{grad}(\rho_\alpha)+\boldsymbol{w}_\alpha\cdot\nabla(\rho_\alpha)+\rho_\alpha\operatorname{div}(\boldsymbol{v}_\alpha)+\rho_\alpha\nabla_{\boldsymbol{n}}\cdot(\boldsymbol{w}_\alpha)\right]}_{\chi_\alpha}$$
$$+\frac{1}{2}\boldsymbol{s}_\alpha\cdot\boldsymbol{\omega}_\alpha\underbrace{\left[\frac{\partial\rho_\alpha}{\partial t}+\boldsymbol{v}_\alpha\cdot\operatorname{grad}(\rho_\alpha)+\boldsymbol{w}_\alpha\cdot\nabla(\rho_\alpha)+\rho_\alpha\operatorname{div}(\boldsymbol{v}_\alpha)+\rho_\alpha\nabla_{\boldsymbol{n}}\cdot(\boldsymbol{w}_\alpha)\right]}_{\chi_\alpha}$$
$$+\varepsilon_\alpha\underbrace{\left[\frac{\partial\rho_\alpha}{\partial t}+\boldsymbol{v}_\alpha\cdot\operatorname{grad}(\rho_\alpha)+\boldsymbol{w}_\alpha\cdot\nabla(\rho_\alpha)+\rho_\alpha\operatorname{div}(\boldsymbol{v}_\alpha)+\rho_\alpha\nabla_{\boldsymbol{n}}\cdot(\boldsymbol{w}_\alpha)\right]}_{\chi_\alpha}$$
$$+\boldsymbol{v}_\alpha\cdot\underbrace{\left[\rho_\alpha\left(\frac{\partial\boldsymbol{v}_\alpha}{\partial t}+\boldsymbol{v}_\alpha\cdot\operatorname{grad}(\boldsymbol{v}_\alpha)+\boldsymbol{w}_\alpha\cdot\nabla(\boldsymbol{v}_\alpha)-\operatorname{div}(\boldsymbol{T}_\alpha)-\nabla_{\boldsymbol{n}}\cdot(\boldsymbol{T}^*_\alpha)-\rho_\alpha\boldsymbol{f}_\alpha\right)\right]}_{\boldsymbol{o}_\alpha-\boldsymbol{v}_\alpha\chi_\alpha\text{ (see B.14)}}$$
$$+\frac{1}{2}\boldsymbol{\omega}_\alpha\cdot\underbrace{\left[2\rho_\alpha\left(\underbrace{\frac{\partial\boldsymbol{s}_\alpha}{\partial t}+\boldsymbol{v}_\alpha\cdot\operatorname{grad}(\boldsymbol{s}_\alpha)+\boldsymbol{w}_\alpha\cdot\nabla(\boldsymbol{s}_\alpha)}_{d^\alpha\boldsymbol{s}_\alpha/dt}\right)-2\operatorname{div}(\boldsymbol{W}_\alpha)-2\nabla_{\boldsymbol{n}}\cdot(\boldsymbol{W}^*_\alpha)-2\rho_\alpha\boldsymbol{g}_\alpha\right]}_{[(\boldsymbol{i}_\alpha-\chi_\alpha\boldsymbol{s}_\alpha)-\boldsymbol{t}_\alpha]\text{ (see B.18)}}$$
$$+\frac{1}{2}\rho_\alpha\boldsymbol{s}_\alpha\cdot\underbrace{\left[\frac{\partial\boldsymbol{\omega}_\alpha}{\partial t}+\boldsymbol{v}_\alpha\cdot\operatorname{grad}(\boldsymbol{\omega}_\alpha)+\boldsymbol{w}_\alpha\cdot\nabla(\boldsymbol{\omega}_\alpha)\right]}_{d^\alpha\boldsymbol{\omega}_\alpha/dt}-\boldsymbol{T}_\alpha:\operatorname{grad}(\boldsymbol{v}_\alpha)-\boldsymbol{W}_\alpha:\operatorname{grad}(\boldsymbol{\omega}_\alpha)$$
$$-\boldsymbol{T}^*_\alpha\cdot\nabla:(\boldsymbol{v}_\alpha)-\boldsymbol{W}^*_\alpha:\nabla(\boldsymbol{w}_\alpha)+\operatorname{div}(\boldsymbol{\phi}_\alpha)+\nabla_{\boldsymbol{n}}\cdot(\boldsymbol{\phi}^*_\alpha)=\rho_\alpha r_\alpha+\epsilon_\alpha.$$

Adding and subtracting the term $\frac{1}{2}\boldsymbol{\omega}^{\alpha}\cdot\rho_{\alpha}\frac{d\boldsymbol{s}^{\alpha}}{dt}$ on the left hand side of the above equation, one obtains the internal energy balance

$$\rho_{\alpha}\frac{d^{\alpha}\varepsilon_{\alpha}}{dt}+\operatorname{div}(\boldsymbol{\phi}_{\alpha})+\nabla_{\boldsymbol{n}}\cdot(\boldsymbol{\phi}_{\alpha}^{*})-\boldsymbol{T}_{\alpha}^{T}:\operatorname{grad}(\boldsymbol{v}_{\alpha})-\boldsymbol{W}_{\alpha}^{T}:\operatorname{grad}(\boldsymbol{\omega}_{\alpha})-\left(\boldsymbol{T}_{\alpha}^{*}\right)^{T}:\nabla(\boldsymbol{v}_{\alpha})$$
$$-\left(\boldsymbol{W}_{\alpha}^{*}\right)^{T}:\nabla(\boldsymbol{\omega}_{\alpha})+\omega_{\alpha}\cdot[(\boldsymbol{i}_{\alpha}-\chi_{\alpha}\boldsymbol{s}_{\alpha})-\boldsymbol{t}_{\alpha}]+\boldsymbol{v}_{\alpha}\cdot(\boldsymbol{o}_{\alpha}-\boldsymbol{v}_{\alpha}\chi_{\alpha})$$
$$+\chi_{\alpha}\left(\varepsilon_{\alpha}+\frac{1}{2}\boldsymbol{v}_{\alpha}\cdot\boldsymbol{v}_{\alpha}+\frac{1}{2}\boldsymbol{s}_{\alpha}\cdot\boldsymbol{\omega}_{\alpha}\right)+\frac{1}{2}\rho_{\alpha}\left(\boldsymbol{\omega}_{\alpha}\cdot\frac{d^{\alpha}\boldsymbol{s}_{\alpha}}{dt}-\boldsymbol{s}_{\alpha}\cdot\frac{d^{\alpha}\boldsymbol{\omega}_{\alpha}}{dt}\right)=\rho_{\alpha}r_{\alpha}+\mathfrak{e}_{\alpha}. \quad \text{(B.22)}$$

In this equation $\mathfrak{G}_{\alpha}=\frac{1}{2}\rho_{\alpha}\left(\boldsymbol{\omega}_{\alpha}\cdot\frac{d^{\alpha}\boldsymbol{s}_{\alpha}}{dt}-\boldsymbol{s}_{\alpha}\cdot\frac{d^{\alpha}\boldsymbol{\omega}_{\alpha}}{dt}\right)$ is the micromorphic spin production of constituent α, but for a micro-polar continuum it vanishes. Thus, $\mathfrak{G}_{\alpha}$ will be null in the above equation. Considering such an omission, for the solution one has

$$\rho\frac{d\varepsilon}{dt}+\operatorname{div}(\boldsymbol{\phi})+\nabla_{\boldsymbol{n}}\cdot(\boldsymbol{\phi}^{*})-\boldsymbol{T}^{T}:\operatorname{grad}(\boldsymbol{v})-\boldsymbol{W}^{T}:\operatorname{grad}(\boldsymbol{\omega})-\left(\boldsymbol{T}^{*}\right)^{T}:\nabla(\boldsymbol{v})$$
$$-\left(\boldsymbol{W}^{*}\right)^{T}:\nabla(\boldsymbol{\omega})-\boldsymbol{\omega}\cdot\boldsymbol{t}=\rho r, \quad \text{(B.23)}$$

where

$$\sum_{\alpha=1}^{N}\mathfrak{e}_{\alpha}=0,\quad \mathfrak{G}=\frac{1}{2}\rho_{\alpha}\left(\boldsymbol{\omega}_{\alpha}\cdot\frac{d^{\alpha}\boldsymbol{s}_{\alpha}}{dt}-\boldsymbol{s}_{\alpha}\cdot\frac{d^{\alpha}\boldsymbol{\omega}_{\alpha}}{dt}\right)=0$$
$$\rho\, r=\sum_{\alpha=1}^{N}\left(\rho_{\alpha}r_{\alpha}+\boldsymbol{u}_{\alpha}\cdot\rho_{\alpha}\boldsymbol{f}_{\alpha}+\boldsymbol{z}_{\alpha}\cdot\rho_{\alpha}\boldsymbol{g}_{\alpha}\right),\quad \rho\varepsilon=\sum_{\alpha=1}^{N}\left(\rho_{\alpha}\varepsilon_{\alpha}+\frac{1}{2}\rho_{\alpha}\boldsymbol{u}_{\alpha}\cdot\boldsymbol{u}_{\alpha}+\frac{1}{2}\rho_{\alpha}\boldsymbol{s}_{\alpha}\cdot\boldsymbol{z}_{\alpha}\right),$$
$$\boldsymbol{\phi}=\sum_{\alpha=1}^{N}\left[\boldsymbol{\phi}_{\alpha}-\boldsymbol{u}_{\alpha}\boldsymbol{T}_{\alpha}^{T}-\boldsymbol{z}_{\alpha}\boldsymbol{W}_{\alpha}^{T}+\left(\rho_{\alpha}\varepsilon_{\alpha}+\frac{1}{2}\rho_{\alpha}\boldsymbol{u}_{\alpha}\cdot\boldsymbol{u}_{\alpha}+\frac{1}{2}\rho_{\alpha}\boldsymbol{s}_{\alpha}\cdot(\boldsymbol{z}_{\alpha}-\boldsymbol{\omega})\right)\boldsymbol{u}_{\alpha}\right],$$
$$\boldsymbol{\phi}^{*}=\sum_{\alpha=1}^{N}\left[\boldsymbol{\phi}_{\alpha}^{*}-\boldsymbol{u}_{\alpha}\boldsymbol{T}_{\alpha}^{T}-\boldsymbol{z}_{\alpha}\boldsymbol{W}_{\alpha}^{T}+\left(\rho_{\alpha}\varepsilon_{\alpha}+\frac{1}{2}\rho_{\alpha}\boldsymbol{u}_{\alpha}\cdot\boldsymbol{u}_{\alpha}+\frac{1}{2}\rho_{\alpha}\boldsymbol{s}_{\alpha}\cdot(\boldsymbol{z}_{\alpha}-\boldsymbol{\omega})\right)\boldsymbol{w}_{\alpha}\right].$$

Here, $\boldsymbol{z}_{\alpha}=\boldsymbol{\omega}_{\alpha}-\boldsymbol{\omega}$ was used to obtain the relations above.

Entropy

Considering the whole solution as a constituent, for the solution entropy balance the variables in (B.2) are defined as follows:

$$\psi = \rho s, \quad \boldsymbol{\Gamma} = \boldsymbol{\mathfrak{E}}, \quad \boldsymbol{\Gamma}^* = \boldsymbol{\mathfrak{E}}^*, \quad \mathfrak{s} = \rho\eta, \quad \mathfrak{p} = \rho\sigma.$$

Hence, the entropy balance of the solution is given by

$$\rho\sigma = \frac{\partial \rho s}{\partial t} + \operatorname{div}\left(\rho s \boldsymbol{v} + \boldsymbol{\mathfrak{E}}\right) + \nabla_{\boldsymbol{n}} \cdot \left(\rho s \boldsymbol{w} + \boldsymbol{\mathfrak{E}}^*\right) - \rho\eta \geq 0. \tag{B.24}$$

Using (B.5) and (B.7), one obtains

$$\rho\sigma = \rho\frac{ds}{dt} + \operatorname{div}\left(\boldsymbol{\mathfrak{E}}\right) + \nabla_{\boldsymbol{n}} \cdot \left(\boldsymbol{\mathfrak{E}}^*\right) - \rho\eta \geq 0. \tag{B.25}$$

where

$$\rho\, s = \sum_{\alpha=1}^{N} \rho_\alpha\, s_\alpha, \quad \rho\eta = \sum_{\alpha=1}^{N} \rho_\alpha \eta_\alpha, \quad \rho\sigma = \sum_{\alpha=1}^{N} \rho_\alpha \sigma_\alpha$$

$$\boldsymbol{\mathfrak{E}} = \sum_{\alpha=1}^{N} \left(\boldsymbol{\mathfrak{E}}_\alpha + s_\alpha \boldsymbol{u}_\alpha\right), \quad \boldsymbol{\mathfrak{E}}^* = \sum_{\alpha=1}^{N} \left(\boldsymbol{\mathfrak{E}}^*_\alpha + s_\alpha \boldsymbol{\varpi}_\alpha\right).$$

References

[1] K. Hutter, K. Jöhnk, *Continuum Methods of Physical Modeling* (Springer, Berlin, 2010).

[2] S. Nair, *Introduction to Continuum Mechanics* (Cambridge University Press, Cambridge, 2011).

[3] C. Papenfuss, W. Muschik, in *Applied Wave Mathematics*, ed. by E. Quak, T. Soomere (Springer, Berlin, 2009), pp. 85.

[4] W. Muschik, C. Papenfuss, H. Ehrentraut, *Concepts of Continuum Thermodynamics* (Kielce University of Technology, Kielce, 1996).

[5] E. Cosserat, F. Cosserat, *Sur la mécanique générale*, C.R. Acad. Sci. **145**, 1139 (1907).

[6] E. Cosserat, F. Cosserat, *Théorie des Corps Déformable* (Hermann, Paris, 1909).

[7] A.C. Eringen, E.S. Suhubi, *Non linear theory of simple microelastic solids I*, Int. J. Eng. Sci. **2**, 189 (1964).

[8] A.C. Eringen, E.S. Suhubi, *Non linear theory of simple microelastic solids II*, Int. J. Eng. Sci. **2**, 389 (1964).

[9] A.C. Eringen, C.B. Kafadar, in *Continuum Physics*, ed. by A.C. Eringen (Academic Press, New York, 1976) pp. 1.

[10] G. Capriz, *Continua with Microstructure* (Springer, Berlin, 1989).

[11] W. Muschik, H. Ehrentraut, C. Papenfuss, in *Geometry, Continua, and Microstructure*, ed. by G.A. Maugin (Hermann, Paris, 1999), pp. 49.

[12] S. Blenk, H. Ehrentraut, W. Muschik, *Statistical foundation of macroscopic balances for liquid crystals in alignment tensor formulation*, Phys. A **174**, 119 (1991).

[13] S. Blenk, H. Ehrentraut, W. Muschik, *Macroscopic constitutive equations for liquid crystals induced by their mesoscopic orientation distribution*, Int. J. Eng. Sci **30**, 1127 (1992).

[14] S. Blenk, H. Ehrentraut, W. Muschik, *A continuum theory for liquid crystals describing different degrees of orientational order*, Liq. Cryst. **14**, 1221 (1993).

[15] W. Muschik, H. Ehrentraut, C. Papenfuss, *Concepts of mesoscopic continuum physics*, J. Non-Equilib. Thermodyn. **25**, 179 (2000).

[16] W. Muschik, C. Papenfuss, H. Ehrentraut, *Sketch of the mesoscopic description of nematic liquid crystals*, J. Non-Newtonian Fluid Mech. **119**, 91 (2004).

[17] W. Muschik, C. Papenfuss, *Mesoscopic continuum mechanics applied to liquid crystals*, Tech. Mech. **30**, 252 (2010).

[18] P. Ván, C. Papenfuss, W. Muschik, *Mesoscopic dynamics of microcracks*, Phys. Rev. E **62**, 6206 (2000).

[19] P. Ván, C. Papenfuss, W. Muschik, *Mesoscopic theory of microcracks*, Arch. Mech. E **55**, 481 (2003).

[20] P. Ván, C. Papenfuss, W. Muschik, *Griffith cracks in the mesoscopic microcrack theory*, J. Phys. A: Math. Gen. **37**, 5315 (2004).

[21] C. Papenfuss, V. Ciancio, P. Rogolino, *Application of the mesoscopic theory to dipolar media*, Tech. Mech. **22**, 132 (2002).

[22] K-C. Chen, *A Mesoscopic Continuum Description of Dry Granular Materials*, J. Non-Equilib. Thermodyn. **33**, 255 (2008).

[23] A. Palumbo, C. Papenfuss, P. Rogolino, *A mesoscopic approach to diffusion phenomena in mixtures*, J. Non-Equilib. Thermodyn. **30**, 401 (2005).

[24] G. T. Mase and G. E. Mase, *Continuum mechanics for engineers* (CRC Press, Boca Raton, 1999).

[25] M. Lai, E. Krempl and D. Ruben, *Introduction to continuum mechanics*, (Elsevier, Oxford, 2010).

[26] G. T. Mase, *Continuum mechanics*, (McGraw-Hill, New York, 1970).

[27] K. Hutter, *The Foundations of Thermodynamics, its Basic Postulates and Implications. A Review of Modern Thermodynamics*, Acta Mech. **2**, 1 (1977).

[28] C. Eckart, *The thermodynamics of irreversible processes I. The simple fluid*, Phys. Rev. **58**, 267 (1940).

[29] C. Eckart, *The thermodynamics of irreversible processes II. Fluid mixtures*, Phys. Rev. **58**, 269 (1940).

[30] J. Meixner, *Zur Thermodynamik der irreversiblen Prozesse in Gasen mit chemisch reagierenden, dissoziierenden and anregbaren Komponenten*, Annalen der Physik. **43**, 244(1943).

[31] J. Meixner, *Zur Thermodynamik der irreversiblen Prozesse*, Z. Phys. Chem. **538**, 235 (1943)

[32] S. R. de Groot and P. Mazur, *Non-Equilibrium Thermodynamics*, (North Holland, Amsterdam, 1963).

[33] I. Prigogine, *Introduction to Thermodynamics of Irreversible Processes*, (Wiley, New York, 1968).

[34] D. Jou, J. Casas-Vázquez and G. Lebon, *Extended Irreversible Thermodynamics*, (Springer, Berlin, 2010).

[35] Y. Wang, K. Hutter, in *Entropy*, ed. by A. Greven, G. Keller, G. Warnecke (Princeton University Press, Princenton, 2003), pp. 57-78.

[36] B.D. Colleman, W. Noll, *An approximation theorem for functionals with applications in continuum mechanics*, Arch. Rat. Mech. Anal. **6**, 355 (1960).

[37] B.D. Colleman, W. Noll, *Foundations of linear viscoelasticity*,Rev. Modern. Phys. **33**, 239 (1961).

[38] B.D. Colleman, W. Noll, *The thermodynamics of elastic materials with heat conduction and viscosity*, Arch. Rat. Mech. Anal. **13**, 167 (1963).

[39] C.A. Truesdell, *Rational Thermodynamics*, (Springer, Berlin, 1984).

[40] C.A. Truesdell, W. Noll, in *The Non-linear Field Theories of Mechanics*, ed. by S.S. Antman (Springer, Berlin, 2004).

[41] A.C. Eringen, *Mechanics of Continua*, (Robert E. Krieger Publishing Company, Huntington, 1980).

[42] I. Müller, *On the entropy inequality*, Arch. Rat. Mech. Anal. **26**, 118 (1967).

[43] I. Müller, *A thermodynamic theory of mixtures of fluids*, Arch. Rat. Mech. Anal. **28**, 1 (1968).

[44] I. Müller, *Thermodynamics of mixtures of fluids*, J. de Mécanique **14**, 267(1975).

[45] I-Shih Liu, *Method of Lagrange multipliers for exploitation of the entropy principle*, Arch. Rat. Mech. Anal. **46**, 131 (1972).

[46] I. Müller, *Thermodynamics*, (Pitman, London, 1985)

[47] I-Shih Liu, *Continuum Mechanics*, (Springer, Berlin, 2002).

[48] R.M. Bowen, *Theory of Mixtures*, pp. 1-127 in Continuum Physics, Vol. 3. ed. by A.C. Eringen, (Academic Press, New York, 1976).

[49] C.A. Truesdell, *Sulle basi della termomeccanica*. Rendiconti Academia dei Lincei **22**, 33 (1957).

[50] I. Müller and T. Ruggeri, *Rational Extended Thermodynamics*, (Springer, Berlin, 1993).

[51] I. Müller and W. Weiss, *Thermodynamics of irreversible processes - past and present*, Eur. Phys. J. H, **37**, 139 (2012).

[52] I. Müller and W. H. Müller, *Fundamentals of Thermodynamics and Applications*, (Springer, Berlin, 2009).

[53] I-Shih Liu, *A solid-fluid mixture theory of porous media*, Int. J. of Eng. Sci. **84**, 133 (2014).

[54] M. C. Reis, Phd thesis with title:*Constitutive modeling of electrochemical systems via the Müller-Liu entropy principle*, (Universidade estadual de Campinas, Campinas, 2014).

[55] J. M. Lee, *Introduction to Topological Manifolds*, (Springer, Berlin, 2010).

[56] G. F. Simmons, *Introduction to Topology and Modern Analysis*, (McGraw-Hill, New York, 1963).

[57] W. Muschik, C. Papenfuss and H. Ehrentraut, *A sketch of continuum thermodynamics*, J. Non-Newtonian Fluid Mech. **96**, 255 (2001).

[58] C. Papenfuss, *The theory of liquids crystals as an example of mesoscopic continuum mechanics*, Comp. Material. Sci. **19**, 45 (2000).

[59] S. Blenk and W. Muschik, *Orientational balances for nematic liquid cristals*, J. Non-Equilib. Thermodyn. **16**, 67 (1991).

[60] K-C. Chen, *Microcontinuum balance equations revisited: The mesoscopic Approach*, J. Non-Equilib. Thermodyn. **32**, 435 (2007).

[61] W. Muschik, H. Ehrentraut, S. Blenk, *Ericksen-Leslie liquid crystal theory revisited from mesoscopic point of view*, J. Non-Equilib. Thermodyn. **20**, 92 (1995).

[62] S. Blenk, H. Ehrentraut and W. Muschik, *Orientation balances for liquid crystals and their representation by alignment tensors*, Mol. Cryst. Liqu. Cryst. **204**, 133 (1991).

[63] H. Ehrentraut, *A unified mesoscopic continuum theory of uniaxial and biaxial liquid crystals*, (Wissenschaft und Technik Verlag, Berlin, 1996).

[64] D. Bothe, W. Dreyer, *Continuum thermodynamics of chemically reacting fluid mixtures*, Acta Mech. **226**, 1757 (2015).

[65] M.C. Reis, A.B.M.S. Bassi, *A continuum thermodynamical approach to electrochemical systems*, J. Math. Chem. **52**, 441 (2014).

[66] M.C. Reis, Y. Wang, A.B.M.S. Bassi, *Toward the thermodynamic modeling of reacting ionic mixtures*, Continuum Mech. Thermodyn. **26**, 753 (2014).

[67] H. Eherntraut, W. Muschik, *An amendment to the second law of thermodynamics*, J. Non-Equilib. Thermodyn. **21**, 175 (1996).

[68] A. Bedford, *On the balance equations for chemically reacting mixtures*, Acta Mech. **30**, 275 (1978).

[69] R. Bowen, *The thermochemistry of a reacting mixture of elastic materials with diffusion*, Arch. Rat. Mech. Anal. **34**, 97 (1969).

[70] R. Bowen, J. Wise, *Diffusion in mixtures of elastic materials*, Int. J. of Eng. Sci. **07**, 689 (1969).

[71] K. Wilmanski, *Lagrangean model of two-phase porous material*. J. Non-Equilib. Thermodyn. **20**, 50 (1995).

[72] K. Wilmanski, *Continuum Thermodynamics. Part I. Foundations* (World Scientific Publishing Company, New Jersey, 2008).

[73] J. R. Carpenter, M. L. Timmermans, *Does Rotation Influence Double-Diffusive Fluxes in Polar Oceans?*, J. Phys. Oceanogr. **44**, 289 (2014).

[74] D. E. O'Reilly, E. M. Peterson, *Self-Diffusion Coefficients and Rotational Correlation Times in Polar Liquids. II*, J. Chem. Phys. **55**, 2155 (1971).

[75] T. L. Hill, *Effect of rotation on the diffusion-controlled rate of ligand-protein association*, Proc. Nat. Acad. Sci. USA, **72**, 4918 (1975).

[76] W. B. Russel, *Brownian motion of small particles suspended in liquids*, Ann. Rev. Fluid Mech. **13**, 425 (1981).

[77] J. Keizer, *Diffusion effects on rapid bimolecular chemical reactions*, Chem. Rev. **87**, 167 (1987).

[78] A. Von Jena, H. E. Lessing, *Rotational Diffusion of Prolate and Oblate Molecules from Absorption Relaxation*, Ber. Bunsenges. Phys. Chem. **83**, 181 (1979).

[79] S. Weiss, *Fluorescence spectroscopy of single biomolecules*, Science **283**, 1676 (1999).

[80] K. I. Morozov, *The translational and rotational diffusion of colloidal ferroparticles*, J. Magn. Magn. Mater. **122**, 98 (1993).

[81] D. Wang, U. Kreutzer, Y. Chung, T. Jue, *Myoglobin and hemoglobin rotational diffusion in the cell*, Biophys. J. **73**, 2764 (1997).

[82] Dor Ben-Amotz and J. M. Drake, *The solute size effect in rotational diffusion experiments: A test of microscopic friction theories*, J. Chem. Phys. **89**, 1019 (1988).

[83] D. Shoup, G. Lipari, A. Szabo, *Diffusion-controlled bimolecular reaction rates. The effect of rotational diffusion and orientation constraints*, Biophys. J. **36**, 697 (1981).

[84] M.C. Reis, C.C.F. Florindo, A.B.M.S. Bassi, *Entropy and its mathematical properties: consequences for thermodynamics*, ChemTexts, **1**, 1 (2015).

[85] C.A. Truesdell, S. Baratha, *The concepts and logic of classical thermodynamics as a theory of heat engines*, (Springer, Berlin, 1977).

[86] W. Muschik, C. Papenfuss, H. Ehrentraut *Alignment tensor dynamics induced by the mesoscopic balance of the orientation distribution function*, Proc. Estonian Acad. Sci. Phys. Math. **46**, 94 (1997).

[87] S. Blenk, W. Muschik, *Mesoscopic concepts for constitutive equations of nematic liquid crystals in alignment tensor formulation*, ZAMM, **74**, T331 (1994).

[88] P. Ván, *Weakly nonlocal irreversible thermodynamics*, Annalen der Physik, **12**, 142 (2003).

[89] V. A. Cimmelli, P. Ván, *The effects of nonlocality on the evolution of higher order fluxes in nonequilibrium thermodynamics*, J. Math. Phys. **46**, 112901 (2005).

[90] P. Ván, *The Ginzburg-Landau equation as a consequence of the Second Law*, Continuum Mech. Thermodyn. **17**, 165169 (2005).

[91] G. McCarty, *Topology: An Introduction with Application to Topological Groups* (Dover Publications, New York, 2011).

[92] D. W. Kahn, *Topology: An Introduction to the Point-Set and Algebraic Areas* (Dover Publications, New York, 1995).

[93] D. W. Kahn, *Elementary Topology* (Dover Publications, New York, 1990).

[94] M. E. Gutin, *An Introduction to Continuum Mechanics* (Academic Press, Cambridge, 1982)